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TRANSACTIONS  
OF THE  
AMERICAN INSTITUTE OF MINING  
AND METALLURGICAL ENGINEERS  
(INCORPORATED)

Vol. 125

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IRON AND STEEL DIVISION  
1937

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PAPERS AND DISCUSSIONS PRESENTED BEFORE THE DIVISION AT THE MEETINGS  
HELD AT CLEVELAND, OCT. 20-22, 1936, AT NEW YORK, FEB. 15-19,  
1937 AND AT BIRMINGHAM, APRIL 7-9, 1937

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## *Notice*

This volume is the tenth of a series containing papers and discussions presented before the Iron and Steel Division of the American Institute of Mining and Metallurgical Engineers since its organization in 1928; one volume each year, as follows:

1928, Iron and Steel Technology in 1928 (later listed as Volume 80 of the TRANSACTIONS); 1929 (vol. 84), 1930 (vol. 90), 1931 (vol. 95), 1932 (vol. 100), 1933, 1934, 1935, 1936 and 1937, TRANSACTIONS of the American Institute of Mining and Metallurgical Engineers, Iron and Steel Division.

This volume contains papers and discussions presented at the meetings at Cleveland, Oct. 20-22, 1936, New York, Feb. 15-19, 1937, and Birmingham, April 7-9, 1937.

Papers on iron and steel subjects published by the Institute prior to 1928 are to be found in many volumes of the TRANSACTIONS of the Institute; in Vols. 37 to 45, inclusive; 47, 50 and 51, 53, 56, 58, 62, 67 to 71, inclusive; 73 and 75. Vol. 67 was devoted exclusively to iron and steel.

Iron and steel papers published in the TRANSACTIONS may be found by consulting the general indexes to Vols. 1 to 35 (1871-1904), Vols. 36 to 55 (1905-1916), Vols. 56 to 72 (1917-1925), and Vols. 73 to 117 (1926-1935), and the indexes in succeeding Year Books.

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## FOREWORD

This volume of the TRANSACTIONS of the American Institute of Mining and Metallurgical Engineers contains papers presented before the Iron and Steel Division at the annual meeting of the Institute in New York in February, 1937, and at the joint meeting with the Institute of Metals Division in Cleveland in October 1936.

Dr. P. D. Merica's interesting Howe Memorial Lecture on Progress in Improvement of Cast Iron and Use of Alloys in Iron introduces the volume and is followed by studies of blast-furnace operations, determination of gases in metals, ingot structure, grain size and the constitution and structure of ferrous metals. Among the papers on blast-furnace practice is one by J. M. Hassler, recipient of the J. E. Johnson, Jr., Award for 1937. The Robert W. Hunt Prize for 1937 was awarded to W. F. Holbrook and T. L. Joseph for their paper on Relative Desulphurizing Powers of Blast-furnace Slags, which appeared in the TRANSACTIONS in 1936 (Volume 120).

One of the activities promoted by the Division's Open Hearth Committee is the Open Hearth Conference. The proceedings of this conference are published separately in a volume entitled: "1937 Open Hearth Proceedings."

Papers dealing with the fundamentals of metallurgy cannot be relegated on any logical basis to one or the other of the two metals Divisions of the Institute, consequently material of interest to members of both Divisions may find its way into the TRANSACTIONS of either of them. Papers of interest to those engaged primarily in ferrous metallurgy may therefore be found also in the Institute of Metals Division Volume of the TRANSACTIONS.

FRANCIS B. FOLEY, *Chairman,*  
Iron and Steel Division.

PHILADELPHIA, PA.  
July 21, 1937

## The Howe Memorial Lecture

THE Howe Memorial Lecture was authorized in April, 1923, in memory of Henry Marion Howe, as an annual address to be delivered by invitation under the auspices of the Institute by an individual of recognized and outstanding attainment in the science and practice of iron and steel metallurgy or metallography, chosen by the Board of Directors upon recommendation of the Iron and Steel Division.

So far, only American metallurgists have been invited to deliver the Howe lecture. It is believed that this lecture would gain in importance and significance were it possible to include metallurgists from other countries, but the Institute has not yet been able to do this on account of lack of special funds to support this lectureship.

The titles of the lectures and the lecturers are as follows:

- 1924 What is Steel? By Albert Sauveur.
- 1925 Austenite and Austenitic Steels. By John A. Mathews.
- 1926 Twenty-five Years of Metallography. By William Campbell.
- 1927 Alloy Steels. By Bradley Stoughton.
- 1928 Significance of the Simple Steel Analysis. By Henry D. Hibbard.
- 1929 Studies of Hadfield's Manganese Steel with the High-power Microscope.  
By John Howe Hall.
- 1930 The Future of the American Iron and Steel Industry. By Zay Jeffries.
- 1931 On the Art of Metallography. By Francis F. Lucas.
- 1932 On the Rates of Reactions in Solid Steel. By Edgar C. Bain.
- 1933 Steelmaking Processes. By George B. Waterhouse.
- 1934 The Corrosion Problem with Respect to Iron and Steel. By Frank. N. Speller.
- 1935 Problems of Steel Melting. By Earl C. Smith.
- 1936 Correlation between Metallography and Mechanical Testing. By H. F. Moore.
- 1937 Progress in Improvement of Cast Iron and Use of Alloys in Iron. By Paul D. Merica.

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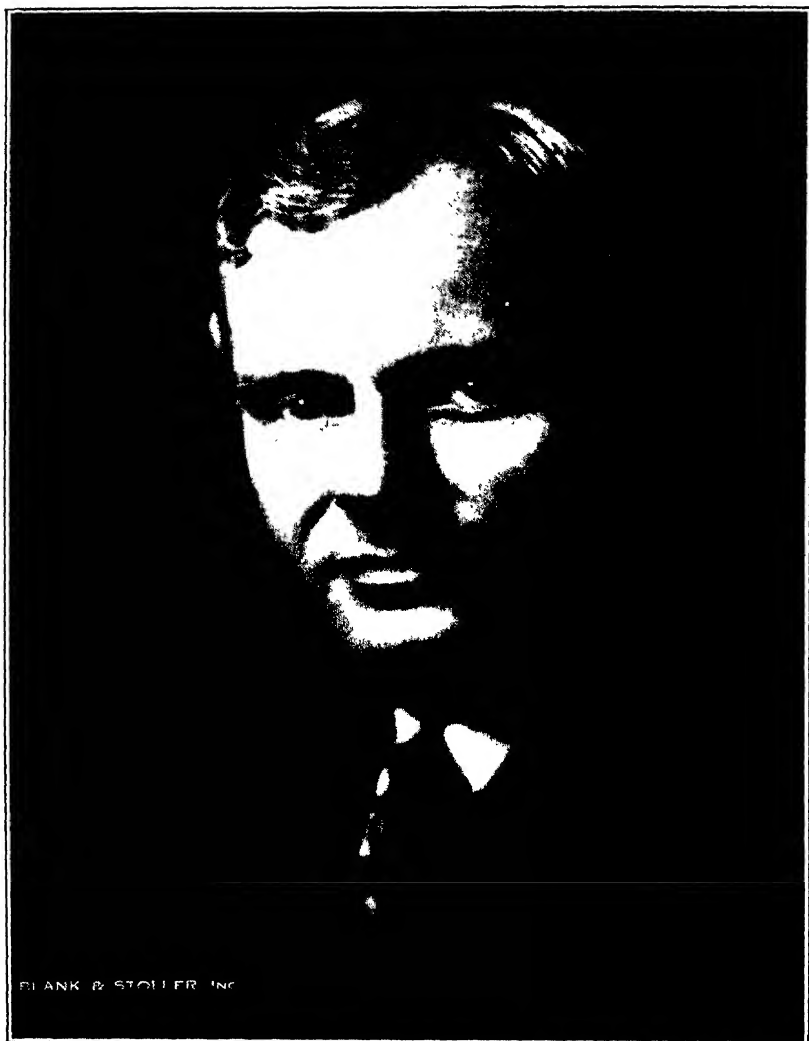
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PAUL D. MERICA

*Henry Marion Howe Memorial Lecturer, 1937*

## Progress in Improvement of Cast Iron and Use of Alloys in Iron

BY PAUL D. MERICA,\* MEMBER A.I.M.E.

(Henry Marion Howe Memorial Lecture†)

THOSE of you who, like myself, have had the privilege of hearing previous Howe Memorial Lectures will note, and I hope without too much disaffection, that for the first time in this series of lectures iron has been chosen as the subject. I feel sure that the predominant choice by previous lecturers of subjects relating to steel has been principally in deference to the well-known interest this subject held for Professor Howe, and that their choice has not reflected any lack of respect for the material, iron. Nevertheless, in the face of this record, I feel some diffidence in introducing this "Cinderella" of materials into the circle of distinguished subjects hitherto treated by Howe lecturers, which is relieved only by the fact that I hope to be able to present some evidence that this Cinderella has at last undergone some of those magical transformations which render her acceptable even in the society of her distinguished sister, steel.

Fortunately I can cite the old master himself in support of my choice of subject and recall to you that Professor Howe by no means overlooked or neglected cast iron in the long course of his metallurgical meditations. Indeed his attention was early arrested by a metallurgical aspect of cast iron which he believed and we still recognize as of the most fundamental importance—namely, the genesis of graphite in gray iron and the means for the control of its quantity and distribution. He made some comments over 20 years ago regarding the nature of J. E. Johnson's oxygenated iron which indicate that even then his thoughts were taking directions which today we are finding it useful to explore in connection with the theory of high-strength iron. Had we had in the subsequent years the continuing benefit of Professor Howe's illuminating consideration of this important subject, our progress in the improvement of cast iron would undoubtedly have been even more rapid.

---

\* Vice-president, International Nickel Co., Inc., New York, N. Y.

† Presented at the New York Meeting, February, 1937. Fourteenth Annual Lecture. Manuscript received at the office of the Institute Feb. 26, 1937.



## ENGINEERING PROPERTIES OF CAST IRON, SUBSTANTIALLY IMPROVED IN RECENT YEARS

It has been a matter of frequent comment that during the early years of the century cast iron, one of the oldest materials of construction, suffered some eclipse of popularity and esteem. Assailed by competition from its more favored sister, steel, which was undergoing rapid and favorable development in many directions—through the art of heat-treatment, through the use of alloys, through the development of the art of welding—it appeared for a long time impossible to find in cast iron those new and hidden resources with which alone this competition could be met. Foundry business was being lost to cast steel, to fabricated steel sheet and plate and to steel forgings.

The last 15 years, however, have witnessed a revival of interest in this somewhat humbled material, accompanied by remarkable progress both in the improvement of its properties and engineering performance as well as in renewed acceptance of it for modern engineering purposes.

That important cast-iron history has been made in recent years can most simply be demonstrated by comparison of the gray-iron specifications of the American Society for Testing Materials for the years 1921 and 1936. In 1921, gray-iron castings were specified to exhibit minimum (arbitration bar) tensile strengths of 18,000 to 24,000 lb. per sq. in., depending upon section thickness. The A.S.T.M. specifications for 1936 call for seven classes of gray iron, requiring minimum tensile strengths from 20,000 to 60,000 lb. per sq. in.

Whereas before the World War the best quality of gray iron\* had a tensile strength no higher than perhaps 15,000 to 20,000 lb. per sq. in., gray iron is today produced in quantity with tensile values from 40,000 to 60,000 lb. per sq. in.; the so-called "high-test" iron. With special care and attention to foundry technique, tensile values even as high as 70,000 to 80,000 lb. per sq. in. are currently obtained. This represents substantial progress.

When substituted for ordinary iron these newer high-strength irons permit savings in section and weight and allow increased load-carrying capacity, since not only their strength but also their elastic moduli are higher. Particularly in the fields of heavy machinery and equipment these irons are making a place for themselves and have in many cases even replaced steel.

But the history of the tensile strength of iron does not tell the whole story of its progress. A great deal of iron is used for purposes for which hardness and abrasion resistance are of primary importance.

---

\* Excepting small amounts of "semisteel," which was just under development and which might have exhibited at that time tensile strengths as high as 30,000 lb. per sq. in.

Fifteen years ago gray iron of machinable quality was not expected in usual sections to possess a hardness of more than about 175 to 225 Brinell. Today alloyed gray iron may be obtained with Brinell hardness of 200 to 275 and even as high as 300 and it can be further heat-treated after machining to 300 to 500 Brinell.

In the field of "chilled" or white-iron castings used for crushing, grinding and rolling equipment, for which maximum hardness and abrasion resistance are sought, the plain chilled iron of 15 years ago offered a "chill" hardness of 400 to 500. Today alloy "chilled" iron may be had with Brinell hardness values of 600 to 700. These harder irons, both gray and chilled, have yielded substantially better wear performance in many industrial applications and have outlasted many times the plain irons which they have replaced.

Finally, alloy cast irons have been developed which possess other properties of engineering value—corrosion resistance, resistance to high temperatures and special magnetic and thermal properties.

Cast iron is today a better and more flexible material than we used to think it and the broadening of its range of physical and mechanical properties, revealed in recent years, has served to redirect to it the attention and the interest of the engineer and the constructor.

An outstanding illustration of the new attitude toward cast iron, and one that has already had well deserved publicity, is the development of the cast-iron camshaft and crankshaft pioneered by the Ford Motor Co., the Campbell, Wyant and Cannon Foundry Co., the Caterpillar Tractor Co. and other prominent manufacturers of automotive and Diesel engines. They have demonstrated that not only can high-quality iron be substituted with substantial economy for the heat-treated steel formerly used in these vital engine parts, but with entire safety as well, together with advantage from the standpoint of service life. Cast iron is certainly no longer a Cinderella in the automotive industry!

### HOW MUCH "HIGH-DUTY" IRON IS USED TODAY?

It is natural to inquire concerning the extent to which these newer "high-duty" and alloy irons are today used. Mr. Steinebach, of *The Foundry*,\* has recently estimated that there may have been produced in this country during 1936 about 10,000,000 tons of gray-iron castings.

From private communications and from information in the files of my own company, the estimate appears conservative that not less than 10,000 tons of alloys† was used in iron castings in the same year, yielding probably between 1,000,000 and 1,500,000 tons of alloy-iron castings.

---

\* Private communication, January, 1937.

† Including alloy content of Mayari and similar synthetic pig irons used by foundries as well as of alloy-steel scrap.

We may therefore consider that between 10 and 15 per cent of iron castings are currently alloyed.\*

Of the 3500 iron foundries estimated to be operating in this country, some 1000 are shown to be users of alloys for a portion at least of their castings production. Of many of these the proportion of alloy-iron production is high—as much as one-third. Some, particularly those serving the automotive industry, produce principally alloy iron. It is estimated, for example, that over 90 per cent of automotive engine castings are of alloy iron, and the whole automotive industry probably consumes half of the alloy iron produced today.

When we consider that the alloy-iron industry has attained these proportions in less than a dozen years and recall that the alloy-steel ingot production in this country after many more years of development constitutes perhaps 6 per cent of the total steel ingot production, we may appreciate that alloy irons have had a speedy “bringing up.”

It is even more difficult to estimate the volume of production of high-test gray iron as distinct from alloy iron, since this term is of somewhat flexible definition anyway and much high-test iron is also alloy iron. But it is certain that between the various cupola processes, the air furnace, the electric furnace and rotary furnaces this volume is substantial, particularly among those foundries supplying castings to the principal engineering fields, and is probably in excess of 500,000 tons. It is perhaps not generally appreciated that there are about 200 electric furnaces operating on iron in this country and supplying perhaps 500,000 tons of castings, of which a substantial portion is of high-test quality.

It will probably be accepted as a conservative guess that, including alloy iron, 15 per cent of all iron (excluding malleable) today is of improved or high-duty quality, in the general sense of the term.

### STRUCTURE AND CHARACTERISTICS OF IRON

The improvement in gray iron in recent years has taken many different directions but I wish to comment particularly on three major developments which have made large contribution to its progress: (1) improvement in melting technique and casting control; (2) the use of alloys; and (3) the application of heat-treatment. These all play important roles in modern irons; sometimes singly but more frequently in association with each other. A Diesel-engine cylinder liner, for example, may be made of high test† iron with alloy additions and hard-

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\* Malleable iron is not included in these estimates but some of the alloys sold were used in chilled iron.

† I shall use the term “high-test” iron to denote its common reference to gray iron of higher strength produced by any of the several melting and casting techniques which have been developed.

ened by heat-treatment. Its properties are the result of the combined influence of the three methods of improving iron.

Before however, discussing the manner in which the application of each of these methods serves to enhance the quality of iron, I must recall to you briefly the structural characteristics of this material. Iron is a more complex material than steel and in consequence the response of iron to variations in composition and of thermal history is far less simple than that of steel.

Structurally gray iron is usually described as steel with intermixed graphite; a steel matrix broken up and weakened by graphite flakes. The size, shape and distribution of these flakes determine and limit its strength, and the matrix or metallic base of the iron determines primarily its hardness. The character of the graphite flakes and that of the matrix both respond independently, and often quite sensitively, to alterations in composition, as well as to additions of alloys and to variations in thermal history and of melting procedure. These responses are sometimes additive, tending to improve or impair the properties of the iron; sometimes they tend to neutralize each other. Iron is not a simple material to control! But fortunately it turns out to be a pretty effective and sensitive instrument for the production of physical properties—after the technique for its manipulation has been mastered!

The most obvious way to improve and strengthen gray iron, and the cheapest, is to reduce the amount of weak graphite flakes. This can be done by lowering the carbon content of the iron, or its silicon content, below the usual percentages. This is in fact the principal theme of that first group of improvement methods to which I shall later refer. We shall see that much can be and has been accomplished in this direction.

One hurdle, however, has always inconveniently early barred this path. When the carbon or silicon content of an iron casting are too far lowered in search of higher properties, the portions that cool rapidly—thin sections, edges or corners—fail to graphitize and in them hard and unmachinable carbides make their appearance. The resulting casting, although exhibiting better physical properties in its heavier, gray sections, is “chilled,” white and unmachinable in its lighter sections.

This tendency of gray iron to “spill over” into white iron—to revert, incidentally, not to the stable but to the unstable form—definitely limits the level of mechanical properties obtainable in gray and machinable plain iron and has been a principal cause of the retardation of progress in the metallurgical development of this material.

This behavior of iron may be demonstrated nicely in the well-known “step-bar” test, by observing the structure and hardness of irons of different composition in the different sections of a step-bar casting (Fig. 1). If we attempt to increase the hardness of plain iron in 1-in. section much beyond its natural limit of perhaps 200, by lowering the

silicon (or the carbon) content, the thinner sections become white and unmachinable.

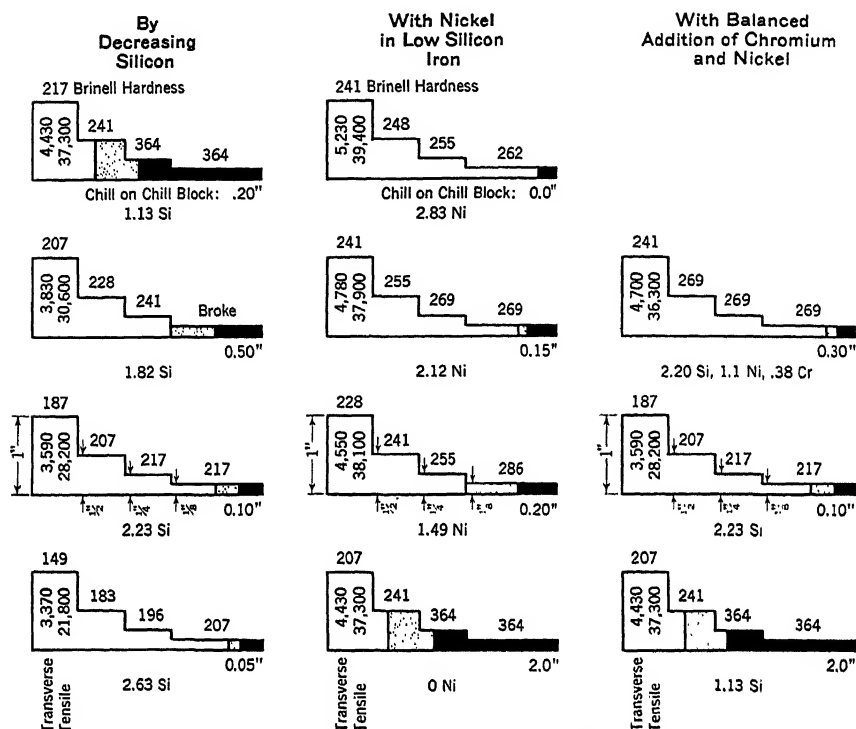


FIG. 1.—HARDENING GRAY IRON IN STEP-BAR CASTINGS.

By decreasing the silicon content or by addition of either nickel or chromium and nickel in balanced proportion.

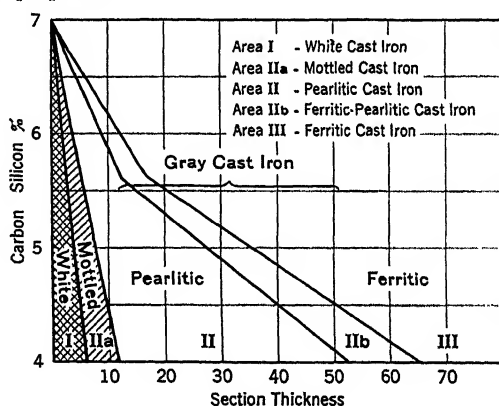


FIG. 2.—STRUCTURAL DIAGRAM FOR CAST IRON ACCORDING TO GREINER AND KLINGENSTEIN.

The limits of composition and of casting section thickness within which iron remains gray and machinable are well shown in the Maurer

structural diagram for cast iron as well as that of Greiner and Klingenstein\* which is here reproduced (Fig. 2). The best plain irons are of full pearlitic structure and are shown therein, bordered on the one hand by soft and weak iron of ferritic structure, and on the other by unmachinable irons of mottled or white structure. If the properties of the pearlitic irons lying in the areas just bordering on mottled iron are explored, values will be found ranging from 25,000 to 35,000 lb. per sq. in. in tensile strength and from 175 to 225 in Brinell hardness. In irons produced by modern methods of composition and melting control, these values of tensile strength may be found increased to 40,000 to 50,000 lb. per sq. in. and, of hardness, to 200 and 230.

These are about the optimum properties of plain gray iron—experience has indicated that—and in order to improve upon them we must have recourse to alloys. They permit us to extend still further the useful working limits of mechanical properties in gray iron, and to raise the level of their properties beyond those possible in plain foundry iron.

Finally, the application of heat-treatment to gray iron yields still further enhancement, particularly of its hardness and resistance to wear.

Let us review for a moment these three methods for the manipulation of cast iron and its properties.

#### IMPROVEMENT OF IRON BY MODIFICATION OF MELTING AND CASTING TECHNIQUE

It is natural that in seeking improvement in the strength of iron, metallurgists should have turned first to methods familiar to them and have sought to reduce the amount of weakening graphite. And why not do this simply by reducing the total carbon content of iron through the use of steel additions in the cupola? The first response to this natural query was "semisteel"—a response which has played a most important role in the subsequent development of high-strength iron.

In its earlier years—from about 1910 until the '20's—semisteel was usually produced with moderate steel additions in the cupola†—from 10 to 30 per cent—and its tensile strength ranged from 20,000 to 30,000 lb. per sq. in. During the '20's it underwent rapid development; the percentage of steel was increased and with it the strength of the resulting product.

But other developments were also taking place. Difficulties were early encountered in the control of cupola operations when melting steel and producing low-carbon iron, and they suggested the advantages of the electric furnace, of which many were installed in foundries in this country beginning in the '20's. It was found possible in this furnace

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\* *Stahl und Eisen* (1925) 45, 1173.

† Some foundries even then were using higher percentages; McPherran reports using 60 per cent of steel as early as 1913.

accurately to control composition, and electric-furnace gray iron could be offered of low carbon content possessing tensile strength varying from 35,000 to 50,000 lb. per sq. in. In the course of his studies of electric-furnace iron, Elliott<sup>1</sup> came to a realization of the favorable effect of "superheating" of molten iron upon its quality and characteristics, and he noted that superheated electric iron required more silicon than ordinary iron. Piwowarsky<sup>2</sup> later was able to show that the superheating of iron, at least within certain temperature limits, not only refined its graphite structure but increased its combined carbon content as well. The idea was thus introduced of refining the graphite structure of iron as well of reducing the amount of graphite.

Discussion of the reason for this useful refining effect of superheating led to a theory of the production of fine graphite structure in iron; namely, that it was necessary to eliminate from the molten iron undissolved graphite residues, which served as crystallization nuclei for the formation and growth, during solidification, of coarse graphite flakes.

This theory appeared to explain also the improved results being obtained not only in the electric but also in the air furnace. Heating molten iron for longer periods at lower temperatures yielded beneficial structural results and strength comparable with those after short periods at higher temperatures.<sup>3</sup>

The graphite-residue theory was also probably at the bottom of the reasoning which led to the development of the so-called "inoculation" or ladle graphitizing methods developed at the Ross-Meehan foundries, and by Coyle.\* If we wish to be sure that an iron inherits no graphite from its former state, why not choose an iron which is normally white in structure? In these methods cupola charges are so chosen as to yield a "tapping" iron of low silicon and of moderately low carbon content, which would be white if cast. Graphitizing agents, however, are added in the ladle just before pouring the molds, which render the resulting iron gray and machinable. These agents may be calcium silicide, as in the Meehanite process, or ferrosilicon (Fig. 3).

An attempt in a slightly different direction to utilize low-carbon irons was that comprised in the Lanz process,<sup>4</sup> in which irons of about 3 per cent carbon and 1 per cent silicon, or less, were graphitized by casting into heated molds. It was these products which for a time carried the name of "pearlitic" irons and which demonstrated anew those advantages of low silicon and carbon content in iron which had long ago been pointed out by Keep.

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<sup>1</sup> References are at the end of the paper.

\* Mr. Jerome Strauss has related the interesting fact that he witnessed as early as 1920 the use of ferrosilicon by Outerbridge in Philadelphia in "inoculating" ladle iron for the production of lathe bed castings.

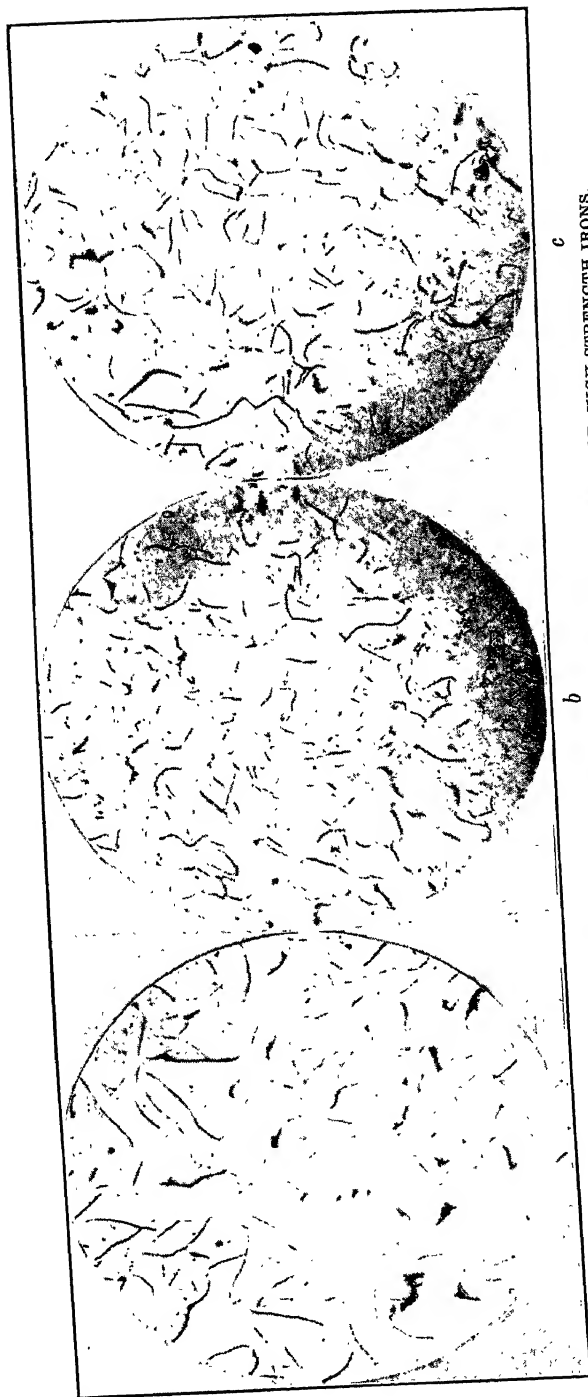


FIG. 3.—GRAPHITE STRUCTURE AND TENSILE STRENGTH OF PLAIN AND OF HIGH-STRENGTH IRONS.

- a.* Plain cast iron having tensile strength of 25,000 lb. per sq. in.  
*b.* High-strength iron having tensile strength of 49,200 lb. per sq. in.  
*c.* High-strength iron having tensile strength of 58,700 lb. per sq. in.  
*b* and *c* are of substantially identical composition and structure but exhibit different tensile strengths.  
Original magnification 100; reduced  $\frac{1}{3}$  in reproduction.



As a consequence of the progressive realization by foundrymen of the valuable roles played by these various factors of foundry melting practice in the improvement, and notably in the strengthening of iron, wide use is being made of them today in the production of high-test iron. The actual methods of high-test iron production have not yet suffered restrictive standardization and their detail varies in the different foundries producing it. The most important single factor is certainly reduction of carbon content—from its usual figure in gray iron of from 3.20 to 3.40 per cent to a range between 2.50 and 3.0 per cent. These irons are produced from electric furnace, air furnace, rotary furnace and the cupola; and the reduction of carbon content, particularly in cupola operations, is secured by steel additions up to 60 and 80 per cent.

Ladle graphitizing is commonly practiced, and superheating as well, particularly in the electric furnace. Cupola-melted steel-bearing charges probably yield an important portion of the production of high-test iron today and ladle graphitization is widely practiced in connection with such operations.

Tensile strength values of 40,000 to 50,000 lb. per sq. in. are obtained readily without the use of alloy hardeners,\* and their use is not normally justified from the cost standpoint in securing strength values within this range, except when other considerations are also involved.

A most important factor in securing these gratifying results is that of better foundry control of composition and melting practice, a factor emphasized by Emmel<sup>6</sup> and others. The comment is often made that without a "high-test" foundry there is no "high-test" iron! The successful everyday production in a foundry of iron of 40,000 to 50,000 lb. per sq. in. in tensile strength is a good testimonial to the character of the technical control there exercised!

Although these various methods have permitted substantial enhancement in the strength properties of gray iron, it does not follow that the simple theories advanced to explain these pleasant results are necessarily adequate for this purpose. Refinement of graphite structure in gray iron may usually be a result of the undercooling of molten iron below the graphite eutectic temperature, but the results of recent investigations indicate pretty clearly that this failure to undercool is not solely caused by the presence of graphite residues in the molten iron.

The significance of the presence of other crystallization nuclei in molten iron, such as inclusions of oxides, sulphides and silicates, the so-called "silicate slimes" of von Keil,<sup>6</sup> has become more and more apparent, and we can in some cases trace a pretty clear connection between the production or the elimination of such inclusions and the coarsening or refining of graphite.<sup>7</sup>

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\* But alloys such as ferrosilicon or calcium silicide may be used for ladle graphitization even in irons of this range of strength.

The explanation of many of the puzzling aspects of superheated iron and of the response of iron to alloy additions may well be found also to be closely related to the character of the inclusions affected by such treatments.<sup>8</sup> It is not unlikely that the value of such elements as calcium and silicon in connection with ladle graphitization methods may be related to their deoxidizing action and to the consequent formation of fine disperse inclusions.

It must also be noted that the character of the graphite structure is not always the sole or even the principal determinant of strength, as it has been rather simply assumed to be in the past. Most foundries producing high-test iron have encountered puzzling instances of irons of substantially similar analysis and of similar graphite structure, which yet possessed widely different strength values, and I present a micrographic illustration of this sort (Fig. 3). When we distinguish more carefully between primary austenitic grain-structure refinement and graphite-flake refinement, and consider them as independently effective features of iron structure and when, in addition, we take into account more intelligently the effect of the presence or absence of the many types of inclusions which infest iron, we shall be well on the road to a clearer explanation of what we do when we make high-test iron.

#### EFFECT OF ALLOYS ON IRON

The idea of using alloys in cast iron cannot be claimed for modern times. One Hickling, as early as 1799, took out a British patent covering the construction of hollow vessels of nickel cast iron. And, beginning as early as 1900, we have had sufficient information available concerning the effect of certain alloys upon iron to permit a realization of their economic value to foundries.

There was not, however, a real market for high-quality iron until after the World War, when the automotive industry began to seek better iron and to stimulate foundries to improve their product. Furthermore, it is no secret that the industrial development of the foundry use of alloys has had a pretty intimate association with a natural ambition on the part of alloy producers to develop a market for their product. And this organized interest in

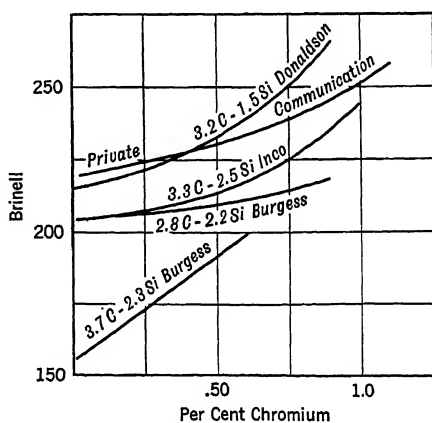


FIG. 4.—GRAPHIC PICTURE OF PUBLISHED DATA ON EFFECT OF CHROMIUM ON BRINELL HARDNESS OF GRAY IRON AND ILLUSTRATING VARIATION OF RESPONSE TO CHROMIUM ADDITIONS OF DIFFERENT COMPOSITIONS OF IRON.

support of alloy iron did not develop fully until the years after the war. If it is not too inappropriate for me to suggest it, I should like to point

TABLE 1.—*Summary of Structural Effects of Alloys on Iron*

	Percent- ages Used in Pearlitic Irons, Per Cent	"Chill"	Effect on Carbides (at High Tempera- tures)	Effect on Graphite Structure	Effect on Combined Carbon in Pearlite	Effect on Matrix
Chill-inducing Elements						
Chromium.....	0.15-1.0	Increases <sup>a</sup>	Strongly stabilizes	Mildly refines	Increases	Refines pearlite and hardens
Vanadium.....	0.15-0.50	Increases	Strongly stabilizes	Refines	Increases	Refines pearlite and hardens
Mildly chill-inducing						
Manganese.....	0.30-1.25	Mildly increases	Stabilizes	Mildly refines	Increases	Refines pearlite and hardens
Molybdenum.....	0.30-1.00	Mildly increases	About neutral	Strongly refines	Mildly increases	Refines pearlite and strengthens
Mildly chill-restraining						
Copper.....	0.50-2.0	Mildly restrains	About neutral	About neutral	Mildly decreases	Hardens
Chill-restraining						
Carbon.....		Strongly restrains	Decreases stability	Coarsens	Strongly decreases	Produces ferrite and softens
Silicon.....		Strongly restrains	Decreases stability	Coarsens	Strongly decreases	Produces ferrite and softens
Aluminum.....		Strongly restrains	Decreases stability	Coarsens	Strongly decreases	Produces ferrite and softens
Nickel.....	0.10-3.0	Restrains <sup>b</sup>	Mildly decreases stability	Mildly refines	Mildly de- creases and sta- bilizes at eutectoid	Refines pearlite and hardens
Titanium.....	0.05-0.10	Restrains	Decreases stability	Strongly refines <sup>c</sup>	Decreases	Produces ferrite and softens
Zirconium.....	0.10-0.30	Restrains		About neutral		Produces ferrite and softens

<sup>a</sup> Chill-inducing effect about balances chill-restraining effect of  $1\frac{1}{2}$  parts of silicon or  $2\frac{1}{2}$  parts of nickel.

<sup>b</sup> Chill-restraining effect about one-half that of silicon.

<sup>c</sup> When added in small amounts and particularly when oxygen is also present.

out that the history of alloy iron is not a bad illustration of the metal-lurgical benefits of commercial self-interest and ambition!

The industrial use of alloy iron was initiated, as far as my knowledge goes, in this country and in connection with the sale of Mayari pig iron

to chilled-roll foundries, beginning about 1912. It was not until about 1918, however, that alloys were actually added to cupola gray iron and the use of nickel additions to cylinder iron at the Cadillac foundry appears to have been the first substantial application. During the '20's and subsequently, the use of the alloys nickel, chromium, molybdenum, titanium, vanadium, copper and zirconium was taken up by iron foundries.

Time does not permit me to dwell at length upon the individual effects which these alloys exert upon the structure and properties of iron. Because of the variability in response to alloys, of different grades and composition of iron, the quantitative presentation even of their simpler effects upon hardness, strength and chilling power is difficult. This may be seen from the graphical picture of the various published data on the effect of chromium upon the strength of iron (Fig. 4) and which exhibit considerable divergence. I have therefore preferred instead to present a qualitative picture\* of those features of their relation to iron which are of principal importance for their industrial use in iron (Table 1). No two of these alloys exercise precisely the same effect upon iron; each has its own flavor and individuality—and therein lies much of their potential value to foundry metallurgy, for their very diversity of action gives us greater flexibility of control over the properties of cast iron, particularly when the alloys are used in combination with one another.

There are, however, certain traits common to many of these alloys.

Most of them refine the grain and graphite structure of iron—some of them, such as titanium and molybdenum, quite markedly, as is illustrated in the photomicrographs of plain and titanium-treated iron (Fig. 5).

Most of them build up and stabilize carbon in pearlite form and refine and harden the pearlitic matrix of iron, and may transform it into sorbite and even martensite.

Certain of them—notably chromium and vanadium—act powerfully to induce “chill,” to stabilize carbides and to restrain carbide decomposition into graphite, whether during solidification or in the solid state at higher temperatures.

Some elements promote graphitization and are “chill-restrainers,” and this effect in the case of small additions of elements such as titanium and zirconium may be related to their marked deoxidizing effect. Indeed, the effect of small amounts of certain elements on chill is often reversed when further amounts are added.

Many alloys—such as nickel and copper—refine graphite structure and harden pearlitic matrix and at the same time diminish susceptibility

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\* The American Foundrymen's Association expects to issue shortly a comprehensive report, through one of its committees, on the effects of alloys on iron.

to chill; while molybdenum, with similar effect, increases chilling tendency only mildly.

The value of these alloys in gray iron lies principally in the fact that the various useful effects which they induce in iron—whether building up of combined carbon in pearlitic form, hardening or strengthening—are secured with less increase of chilling susceptibility, and consequently with less sacrifice of machinability, than is possible by other means. If I may use a slightly loose term, it is the capacity of alloys to produce maximum “machinable hardness” in gray iron which is their fundamental contribution to it.

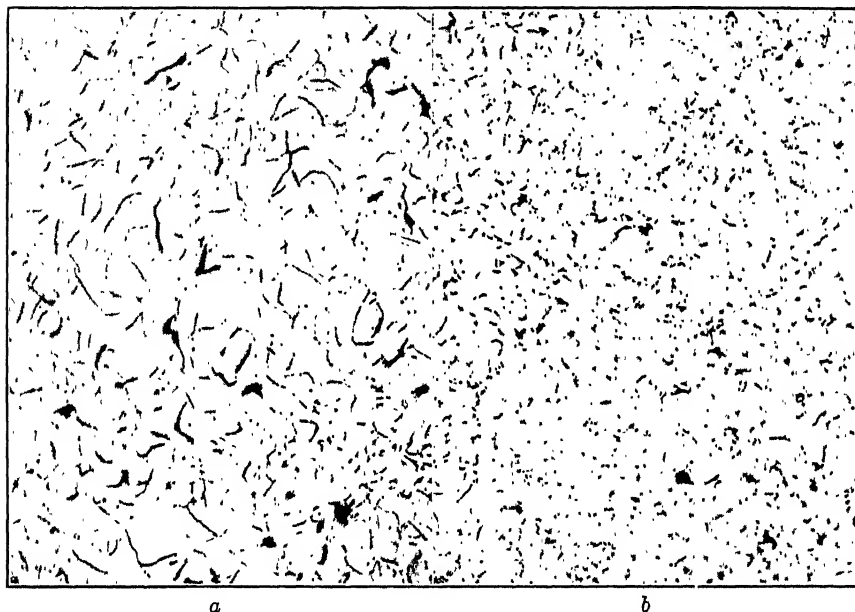


FIG. 5.—REFINEMENT OF GRAPHITE STRUCTURE THROUGH TITANIUM ADDITIONS.  
(Courtesy G. F. Comstock.)

a. Plain cupola iron. b. Same iron with 1 per cent ferrotitanium added.

This contribution is sometimes secured by the addition of a single alloy, and it may be noted that such additions should be made to grades of iron suited to the alloy in question. Thus chromium, a chill-inducing element, is best added to a high-silicon iron, and nickel, a chill-restraining element, to a low-silicon iron. More frequently alloys are added to iron in combinations of two or even more, and such combinations are generally made in what is called a “balanced ratio”—that is, balanced with respect to the effect of the combined alloys upon susceptibility to chill. Balanced additions, for example of chromium and nickel, of copper and chromium, of vanadium and titanium, do not alter the chilling power of the iron but nevertheless refine its structure and harden its matrix.

These structural effects are again well illustrated by the results of step-bar tests of plain and alloy iron (Fig. 1). In plain iron the Brinell hardness in 1-in. section could not be increased to 217 without rendering even a  $\frac{1}{2}$ -in. section difficultly machinable. In either a low-silicon iron with addition of nickel or a 2 per cent silicon iron with "balanced" chromium-nickel addition, the hardness of 1-in. section could be increased to 241 with but faint evidence of chill even in the  $\frac{1}{8}$ -in. section. These same effects are portrayed in a somewhat different manner in the diagram of another figure (Fig. 6). It is difficult in a plain iron to choose a composition which will be reasonably hard and strong in heavy section yet gray and machinable in light ones. Even with moderate alloy

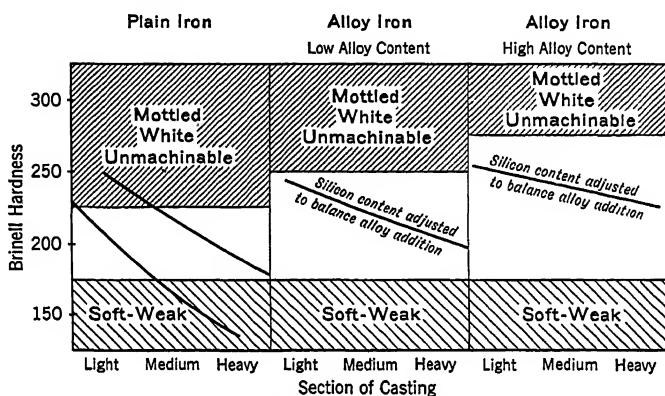


FIG. 6.—DIAGRAMMATIC PRESENTATION OF EFFECT OF ALLOYS IN WIDENING RANGE OF MECHANICAL PROPERTIES IN IRONS WHICH ARE PEARLITIC AND AT THE SAME TIME MACHINABLE.

additions, suitably chosen, this difficulty is relieved, and with larger additions, the level of properties in all sections may be lifted without encroachment of chill and of machining trouble.

In general it proves possible through the use of alloys to increase the tensile strength from 10 to 50 per cent and to raise the level of hardness from about 175 to 225 in plain iron to as high as 275 and even 300, without getting into the range of white or mottled iron with consequent sacrifice of machinability.

Examination of the step-bar casting data will reveal a still further contribution of alloys. Gray iron exhibits variation in the mechanical properties of thick and thin sections and from center to surface of a heavy casting section. It is afflicted with what has been called "section-sensitivity!" Thus, in the step-bar casting used as illustration the hardness of 2.23 per cent silicon iron varied from 187 in 1-in. section to 217 in  $\frac{1}{8}$ -in. section, a difference of 30 points. The hardness of 2.83 per cent nickel iron varied, however, only 21 points—from 241 to 262. Piowowsky<sup>9</sup> has emphasized the significance of this situation in iron

and has shown that whereas silicon tends to widen the variation of properties with section thickness, many alloys diminish this disparity, as is indicated in the figures reproduced from his results (Figs. 7, 8 and 9).

I call your attention also to a practical illustration of this effect in the results of a survey of bore hardness of an automobile truck cylinder in plain and in alloy iron (Fig. 10). The greater uniformity of the hardness along the bore is evident, as well as its higher level throughout.

We can conclude that alloys not only raise the level of physical properties in gray iron but that also they render their values more uniform

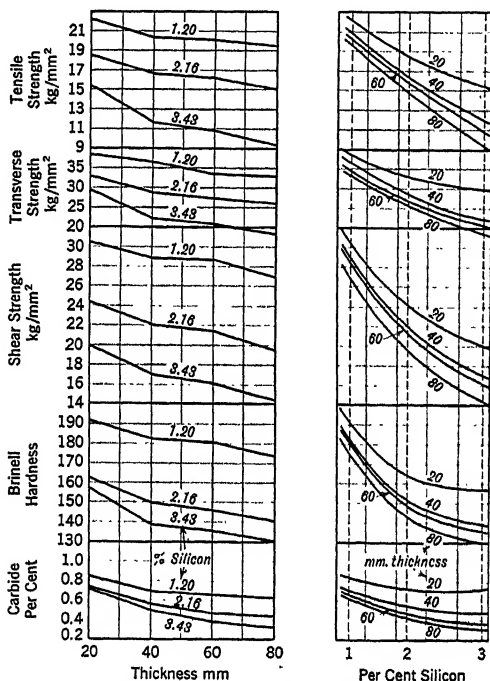


FIG. 7.—EFFECT OF SILICON ON SECTION SENSITIVITY (*Hugo, Piwowarsky and Nipper, 1935*).

throughout the various sections of a casting. This effect is of advantage not alone from the standpoint of machining but also from that of mechanical design, which may with alloy iron be based upon a greater assurance of the structural and mechanical uniformity of iron castings.

The alloys in most common use today in foundry iron are chromium, copper, molybdenum and nickel. Vanadium, titanium, zirconium and tungsten are also coming into more general commercial use and for many uses are gaining favor among foundries.

Other alloys, however, have not been overlooked by foundry metallurgists in their exploration of the means of improving iron. Aluminum, arsenic, antimony, boron, bismuth, calcium, cerium, cobalt, lead, mag-

nesium, tin and others have been investigated, and some of these have been demonstrated to be of definite commercial value in iron for special applications. Thus, aluminum is a necessary component of irons for the nitriding hardening of iron and is sometimes used in heat-resisting irons. Calcium silicide is currently used as a ladle graphitizer in the Meehanite process for the production of high-strength iron. Boron has recently been used for the "hard-surfacing" of iron castings.

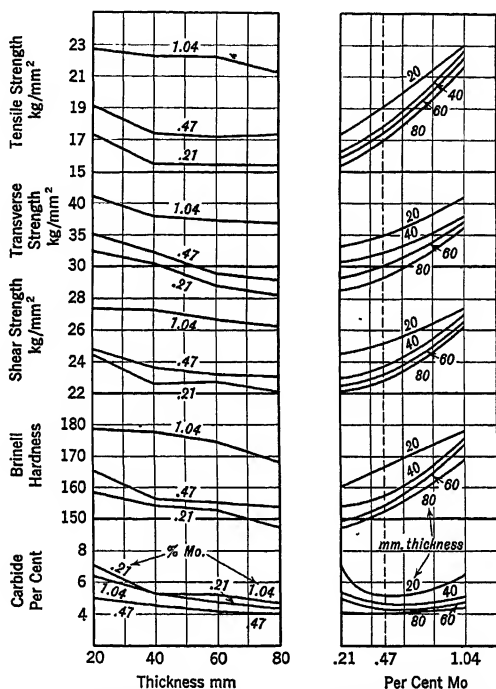


FIG. 8.—EFFECT OF MOLYBDENUM ON SECTION SENSITIVITY (*Hugo, Piwowarsky and Nipper, 1935*).

I should like to mention also that two of the elements occurring in pig iron, silicon and manganese, are themselves frequently added to iron today in ferroalloy form, and it seems probable that more extended use will be made of these alloys. These alloys are cheap and, particularly silicon, appear to exert effects when added in the ladle different from those secured through their introduction in the pig iron itself.

### HEAT-TREATMENT OF IRON

The third method of improving iron, by heat-treatment, recalls an art which has had its major development in application to steel. It may be regarded as adding the finishing touches to the improvement in iron quality already built up by better foundry control and the use of alloys.



Gray iron responds to heat-treatment in a manner quite similar to that of steel, although its tensile strength cannot thereby be increased to anything like the same levels as that of steel.

Plain, unalloyed iron castings of simple shape and design can be heat-treated and are currently so treated today with beneficial result, particularly when the composition of the iron is so chosen as to be of moderate carbon content and of full pearlitic structure. The

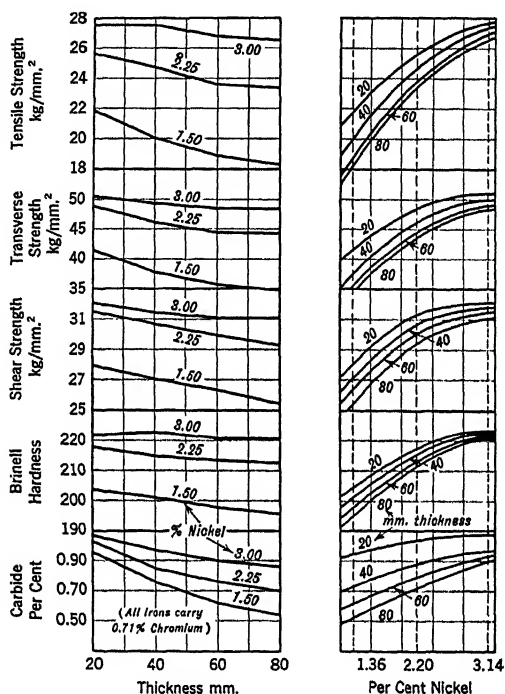


FIG. 9.—EFFECT OF NICKEL-CHROMIUM ON SECTION SENSITIVITY (*Hugo, Piwowarsky and Nipper, 1935*).

major portion of heat-treated gray-iron castings today, however, are of alloy iron.

Just as with steel, many alloys lower the critical cooling rate for hardening and permit better penetration of hardening, particularly after oil quenching. In addition, they allow the quenching operation to be of less drastic character than would be required for the development of equal properties in plain iron.

Most commercial castings which it is desired to heat-treat are of such size as to require alloy iron for effective penetration of hardening, and may be also of such shape as to require moderation of quenching rate in order to avoid thermal damage and distortion during quenching. In the face of either situation recourse is usually had to alloy iron.

Several methods are available for the production of a casting which can be machined and finally heat-treated to a Brinell hardness of 300 to 500. The popular method in this country is to use pearlitic iron with balanced alloy additions and which is machined in the "cast" condition, and then oil-quenched and tempered.

Another method, one that is popular abroad, is to employ enough alloy to render the iron definitely air-hardening. Such an iron may contain, for example, about 4 per cent nickel, 1 per cent manganese and 0.30 per cent chromium, and is hard as cast, but may be softened for machining by annealing at 600° C. After machining at about 300 to 330 Brinell, it may again be hardened, if desired, by an "air-quench" and draw, yielding a Brinell hardness of from 350 to 400.

Two outstanding examples of the application of heat-treatment to gray iron are the die for forming sheet metal and the cylinder liner for

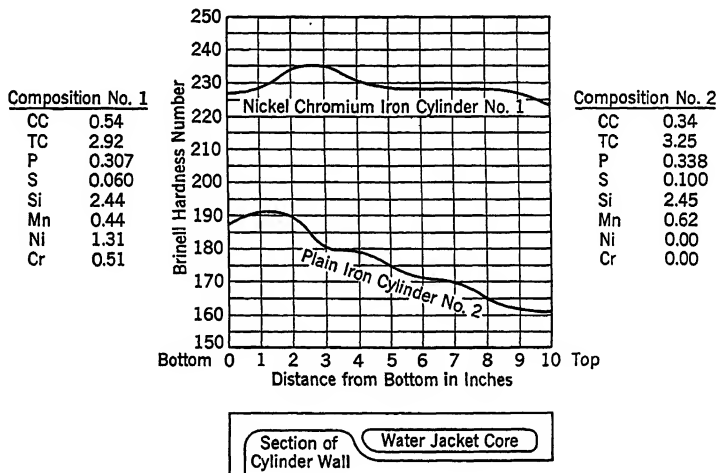


FIG. 10.—EFFECT OF ALLOYS ON UNIFORMITY OF HARDNESS IN DIFFERENT SECTIONS OF AN ENGINE-CYLINDER CASTING.

automotive or Diesel engines. As an illustration of the benefits, from the standpoint of service performance, conferred by heat-treatment of an alloy iron I may cite the fact that heavy forming dies made in chromium nickel iron and after machining, oil-quenching and tempering, have a Brinell hardness of 275 to 350. In this condition they are yielding production records from 5 to 10 times those of plain iron dies, which they have largely replaced.

Chromium, nickel and other alloys, particularly molybdenum, vanadium and manganese, are used in such castings and both single alloy additions and balanced additions are utilized in current foundry practice.

Sometimes it is desired merely to harden a portion of a casting by heat-treatment, as in the automotive camshaft, of which the cam surfaces only need be hard. Such hardening\* is currently practiced by heating the area in question by the oxyacetylene flame and allowing the heated portion to cool in the air.

Although heat-treatment of gray iron is limited today to a few types of castings—principally forming dies, engine cylinders and liners, machinery gears and cams—its practice has become of substantial importance in those fields, and it seems very probable that it will be largely extended in the future.

### INDUSTRIAL APPLICATIONS OF MODERN CAST IRON

Enough has been said to demonstrate that metallurgical progress of recent years has provided us with many aids in the production of cast iron of higher quality and enhanced properties. And if one may be permitted a generalization, which like most generalizations is only partly true, one could suggest that the main theme of the modified melting methods for the production of high-test iron is that of refinement of graphite structure and increase of strength, whereas that of alloy additions is matrix hardening and structural stabilization.

I should now like to turn again to another side of the picture and to review some of the industrial applications of modern high-duty iron. In most industries, but particularly in that of transportation and of power machinery and of machine tools, where there is ever an insistent demand for better materials of construction, these irons are finding increasing application. Their various uses follow engineering patterns closely paralleling the several metallurgical directions in which iron has enjoyed technical progress.

#### *Machinable Gray Iron*

The field of pearlitic, machinable, gray-iron castings was the one in which the stirrings of regenerative progress were first evident, and it remains today the most important single field in which use is made of improved iron. Two objectives are primarily sought in modern pearlitic iron—high strength, on the one hand, and better wear-resistance, on the other. Sometimes the two qualities are required in the same castings, although metallurgically they are not as compatible in gray iron as might be anticipated.

High-strength irons are currently used for such applications as cylinders for Diesel engines and compressors; for locomotive frames and cylinders; in pump casings and liners; for beds and frames of machine tools; for valve bodies and fittings and for mine-hoist drums.

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\* Developed by Campbell, Wyant and Cannon Foundry Co.

Such irons have in many instances replaced steel castings and even forgings—in brake drums, for converter rollers, in gears, for steam-cylinder heads and in flywheel castings. More frequently they have replaced ordinary iron in castings which otherwise would have had to be specified in steel at a higher cost, and have thus permitted increases in capacity without radical and costly change in design.

The most outstanding illustration, of course, has been the substitution of cast iron for steel in forged automobile camshafts and crankshafts for Diesel and other engines. During the past 10 years this substitution has been very general as far as the camshaft is concerned. The use of a high-test iron crankshaft has likewise become common during the past six years for Diesel engines and small engine units operating at intermediate or low speeds. A cast crankshaft is used in the Ford engine but it is a high-carbon steel rather than a cast iron.

In addition to their higher strength, these irons are also more rigid than ordinary gray iron and possess elastic moduli ranging from 15,000,000 to 25,000,000 lb. per sq. in., as compared with values of 12,000,000 to 15,000,000 lb. per sq. in. usually associated with the weaker irons. These higher elastic moduli of the high-test irons are of obvious value in connection with their use for machine tools and many other castings where rigidity approaching that of steel is required.

When strength values in the higher range of 50,000 to 80,000 lb. per sq. in. are required, alloys are generally added to high-test iron. Molybdenum effects a substantial improvement in strength of gray iron, and is today frequently found as a component of high-strength alloy irons in amounts from 0.30 to 1.00 per cent. Nickel is often used, from 1 to 1.5 per cent, sometimes with a higher manganese content up to 1.00 per cent. The combination of 1 per cent nickel and from 0.30 to 1.0 per cent molybdenum is a popular one.

When the engineering consideration is primarily that of wear resistance, the means used to improve iron diverge somewhat from those just indicated for high-strength iron. Graphitic carbon appears to make a definite contribution both to the frictional and to the wear-resisting properties of iron and for many applications of iron requiring these properties it proves undesirable to reduce its amount much below 3.25 per cent. Other means than reduction of carbon content must be used in order to secure the proper structure and hardness required for wear-resistant irons.

It is in this field that alloys have found their greatest popularity. Even in irons of sufficiently high-carbon content—from 3.00 to 3.50 per cent—to afford good frictional properties and wear resistance, a high level of hardness may be secured in machinable alloy irons. The usual range of hardness in which such irons are employed today is from 200 to 250, but in many castings the alloy additions are so chosen as to yield

even higher values—up to 275 and even 300, and by heat-treatment these may be increased up to 500.

These high hardness values are associated with pearlitic or sorbitic structure and are reflected in substantially better wear performance, not only as indicated by laboratory tests but in practical service as well.

Irons of this type find wide application in many industries: as Diesel-engine cylinders and liners, for sheet-metal forming dies, in pump and compressor cylinders and liners, machinery gears, cams and sprockets.

The most prominent examples of the use of wear-resistant alloy iron are to be found in the automotive industry, in the engine cylinder, in brake drums and clutch plates and in camshafts; the majority of these castings are made in alloy iron.

The use of alloy iron in cylinders has permitted the Brinell hardness specified on the cylinder bore to be raised from 160–175 to 190–210. It is generally considered that the harder cylinders have given from 50 to 100 per cent more mileage for the same amount of wear. For heavier cylinders used in buses and trucks, liners are often used and are heat-treated to a bore hardness of from 300 to 500. Eddy<sup>10</sup> reports a 200 per cent increase in effective service life of such liners as compared with unlined cylinder blocks previously used.

For brake drums and the camshafts, alloy iron has replaced the steel originally used. The iron brake drum does not warp under the thermal conditions set up during braking and gives more dependable braking service than steel. Although no service records appear to be available, it is the general impression that these drums also give longer life than steel or plain iron.

The principal objective sought in the substitution of the iron for the steel camshaft was economy, particularly in the saving in forging-die expense as compared with pattern cost. Experience has indicated, however, that the wear resistance of cam bearings and gears has been entirely satisfactory as compared with the same parts of the forged steel camshafts with casehardened cams.

Table 2 shows that there is considerable diversity in the selection of iron compositions for wear-resisting service. And for the same type of castings there are often several different alloy combinations in current use.

We find the alloys sometimes used singly as in the 0.25 to 0.75 per cent chromium irons with increased silicon content and the 0.50 to 2.00 per cent nickel irons with decreased silicon; molybdenum iron with from 0.30 to 1.00 per cent molybdenum is in common use. Combinations of alloys are more frequently used and there is a disposition among some foundry metallurgists to regard combinations of alloys as more economical carriers of their practical values than single additions. When alloy combinations are used, the additions are likely to be made in balanced ratios. And we find chromium-nickel, copper-chromium, molybdenum-

nickel-vanadium, molybdenum-copper and molybdenum-nickel combinations among those which are most commonly used in wear-resisting service.

TABLE 2.—*Illustrative Examples of Compositions of Alloy Iron in Use at Present*

Application	Total C	Si	Mn	Cr	Cu	Mo	Ni
Automotive-cylinder blocks . . . .	3.35	2.20	0.75	0.35			0.70
	3.25	2.25	0.60	0.30			0.25
	3.25	2.00	0.70		0.60		
	3.20	2.15	0.70	0.50		0.50	0.50
	3.25	2.20	0.60	0.50	1.00	1.00	0.20
	3.35	2.00	0.70	0.35			1.75
Brake drums . . . . .	3.30	2.25	0.65	0.30			0.25
	3.25	2.00	0.60		1.00	0.50	
	3.40	2.40	0.70			0.75	1.00
	3.20	1.90	0.70	0.50			1.50
Crankshafts . . . . .	2.50	2.50	1.00			1.00	1.00
	2.80	2.10	0.70			0.60	1.25
	3.00	2.00	0.80			0.75	1.50
	1.50	0.95	0.70	0.45	1.75		
Sheet-metal forming dies . . . . .	3.25	1.50	1.25			0.70	
	3.50	1.50	0.50		V0.20		1.75
	3.00	2.20	0.75	0.35		0.60	2.00
	3.00	1.45	0.90	0.90			3.00
Machine-tool beds . . . . .	3.30	1.60	0.60	0.25		0.20	1.00
	3.00	1.00	0.75	0.35			1.25
	2.90	1.90	0.90				1.50
Hot-strip mill rolls . . . . .	3.00	0.60	0.25			0.35	
	3.00	0.55	0.20	0.25		0.25	2.25
	3.10	0.60	0.20	0.40		0.40	3.50
	3.50	0.90	1.30	2.00			4.50
	3.40	0.60	0.25	1.30		0.40	4.50
Grate bars . . . . .	3.25	2.00	0.70	1.00			
	3.60	1.70	0.50		V0.15		
	3.30	1.50	0.40	0.60			1.50

A highly alloyed chromium-nickel iron, for example, may contain 0.60 per cent chromium and 1.50 per cent nickel, a moderately alloyed iron, 0.30 per cent chromium and 1.00 per cent nickel. For medium and light section castings, small additions of alloy may be used, such as from 0.15 to 0.25 per cent chromium and 0.10 to 0.50 per cent nickel, and

such combinations are popular for smaller automotive cylinders. These smaller chromium-nickel additions may be partly or wholly added in the form of Mayari iron or synthetic alloy pig irons, which are also available.

I do not want to weary you with these recitals of evidence that metallurgists do not always agree, since we are likely to have had ample evidence of this fortunate circumstance at our meetings this week. I shall close these particular lists, therefore, not because they are complete but because they will have illustrated the lack of standardization and the diversity of practice followed today in the choice of alloy irons for wear-resisting service. They will have indicated also a very healthy state of competition among the different alloys and alloy combinations used in iron.

### ALLOYS AS A FOUNDRY AID

The enhancement of the physical properties of iron may properly be regarded as the outstanding result of recent progress in the metallurgy of cast iron. There is another aspect of it, however, which is hardly less important, and which is appreciated particularly among those who carry the responsibility for foundry production. It is the possibility of lowering the cost of finished castings through improvement in the machinability of the iron used as well as through diminished loss of scrapped castings which fail to meet physical property specifications.

Too frequently for his own comfort, the foundryman faces the dilemma of producing castings hard and strong enough to meet his engineering specifications and soft enough to machine economically! Yet failure in either sense may be costly, particularly when it is realized that for every dollar spent on a rough casting there may be from 50¢ to \$10 spent on machining the casting! And this dilemma presents itself to the foundry in many different ways. How to secure good properties in the heavy section of a casting of which a thin section must be machined? How to produce satisfactory thin-section and thick-section castings out of the same foundry iron? How to take care of daily variations in iron composition, which bring trouble in the machine shop?

All those steps which improve the uniformity of structure and of properties in gray iron and increase the level of hardness and strength in readily machinable iron give the foundryman a greater margin of safety in meeting the two requirements of all these problems—requisite hardness and ready machinability. And from what has been shown of the effect of alloys in decreasing section-sensitivity in gray iron and in raising the level of its physical properties, it will not be difficult to understand why alloys have come to be looked upon as “foundry aids” in meeting production problems.

Many foundries are in position to cite examples of savings in machining cost or through reduction of scrapped castings equal to many times

the cost of the alloy additions and this field of foundry use of alloys continues to be a substantial one.

It should be emphasized that much can be done and is being done in the direction of improving section uniformity even without the use of alloys. All of those modifications of melting methods which serve to reduce carbon content and to refine graphite structure aid also in improving the uniformity of structure and properties in sections of different thickness and in consequence aid in meeting production problems. Progressive foundries today are taking advantage of the opportunities offered in this sense by improved production methods as well as by the use of alloys.

### ALLOY IRONS IN MINING AND METALLURGY

The mining and metallurgical industries have not been backward in adopting some of the newer cast irons, and it may be of interest to review briefly some of the applications of such irons in mining equipment and in rolling mills.

The pearlitic, high-test irons just described are employed currently for many parts of mining machinery and rolling-mill equipment for which higher strength and hardness are required—such as crusher frames and shells, compressors and pumps, hoisting drums and hammer frames. There are, however, two rather special types of alloy iron which hold particular interest for engineers in the mining and in the petroleum fields.

*Martensitic White Iron.*—White or chilled iron finds extensive use for the wearing parts of crushing and grinding equipment. Its chill hardness varies within the range from 400 to 500 Brinell, depending largely upon its carbon content. When chromium and nickel are added to such "chillable" iron, its hardness is increased and when the alloy additions are sufficient to render the iron martensitic in structure, this hardness may be as high as 600 to 700. By the aid of special treatment, it has recently been possible in our laboratory to secure Brinell hardness values even in excess of 700 in such an iron.

These martensitic white irons of high hardness exhibit correspondingly enhanced wear resistance and, particularly in crushing and grinding equipment, are today yielding production records and exhibiting service life often many times those of plain chilled iron and sometimes superior to other materials.

Roll segments of chromium-nickel martensitic iron crushed 179,000 tons of coke in equipment in which plain iron segments yielded only 60,000 tons, and coal-pulverizer hammers of the same material were in operation during the grinding of from 2400 to 2900 tons of coal as against 400 to 600 tons with plain iron hammers. Alloy-iron crusher jaws have handled more than 400,000 tons of hard lead-zinc ores and have replaced



alloy-steel jaws which were worn out after crushing about 225,000 tons.

For sand-pump and dredge-pump bodies, for ball-mill and rod-mill liners, for grinding balls, for ore chutes and grizzly disks, and for other similar castings, these martensitic alloy irons have found increasing application.

Similar irons have also been adopted by steel and nonferrous mills for rolls, both for cold and hot-rolling, and alloy rolls have indeed become practically standard for many rolling-mill operations. For cold rolls martensitic chilled iron offers a material, harder than plain chilled iron—from 85 to 90 Shore as against about 65 Shore—and cheaper than forged and hardened steel rolls. Such rolls require substantially less dressing than plain rolls and in tin-plate operations, for example, have been used for 40 to 50 days without redressing as compared with about one week for plain chilled iron. I believe indeed that it may fairly be said that this type of iron has been an important factor in the success of continuous hot-rolling of strip steel, since plain chilled iron is too soft for all but the earlier stages of such operations and hardened steel is subject to heat-cracking and does not retain its hardness under temperature.

Favorite compositions for hard chilled iron are chromium-nickel, molybdenum and chromium-nickel-molybdenum, these alloys falling generally within the following limits: nickel, 2.50 to 6.0 per cent; chromium, 0.50 to 2.50; molybdenum, 0.25 to 1.00. Vanadium and also tungsten aid in securing good chill structure in iron and may be destined to play an important role in future production of martensitic and of alloy chilled irons.

*Corrosion-resistant Iron.*—Not alone the mechanical characteristics of iron have benefited by the progress of recent years. There are other directions, of almost equal interest and significance, in which iron has undergone important development. One of these is corrosion resistance.

When fairly large percentages of certain alloys are added to iron, from 10 to 25 per cent, a group of materials results which is characterized by substantially improved corrosion behavior. These include, for example, the acid-resistant 12 to 15 per cent silicon irons and the high-chromium, high-carbon content irons, which possess excellent oxidation as well as heat resistance. Although derived from cast iron, these alloys are not usually considered as belonging to the cast-iron family.

There is a group of austenitic alloys, however, which can properly be classed with cast iron, since they contain from 2 to 3 per cent carbon, much of it in the form of graphite, and they are gray in structure and machinable. These irons are mechanically similar to gray iron, having a tensile strength of about 25,000 lb. per sq. in. and a Brinell hardness of 125. In other respects they resemble the austenitic steels.

One of the austenitic irons most commonly used today bears the trade name "Ni-Resist," and contains approximately 14 per cent nickel,

6 per cent copper, 1 per cent manganese and 2 per cent chromium together with about .3 per cent carbon. It is used industrially primarily because of its corrosion resistance but also in consequence of certain other special characteristics.

As may be seen from Table 3 in which I have cited representative corrosion-behavior data on Ni-Resist—from both field and laboratory experience—its corrosion rate ranges from one-third, in milder environ-

TABLE 3.—*Corrosion Behavior of Plain and Alloy Iron in Comparison with That of Other Materials*  
(FROM LABORATORY TESTS AND FIELD EXPERIENCE)

Corroding Media and Conditions of Test	Corrosion, Mg. per Sq. Dm. per Day			
	Ni-Resist	Cast Iron	18-8	Bronze
Acetic acid (33 per cent), quiet, unaerated, room temperature.....	17.0	840		18.6 <sup>a</sup>
Hydrochloric acid (1 per cent), quiet, unaerated, room temperature.....	32.5	1,007		41.8 <sup>a</sup>
Sulfuric acid (5 per cent), quiet, unaerated, room temperature.....	37.2	6,880		37.2 <sup>a</sup>
Atmosphere, 1½-yr. test.....	3.5	35.0		
Petroleum refining: acid oil in still, 360° F....	35.0			1,200 <sup>b</sup>
Naphtha, acid-treated, 100° to 110° F.....	97.9	1,598		
Water from kerosene distillate, 105° F.....	201	1,082		1,053 <sup>b</sup>
Water, saturated with H <sub>2</sub> S.....	51	161		
Sodium hydroxide, concentrator, 70 per cent NaOH, 250° F.....	458	1,460	588	
Salt spray, saturated brine, steam and air, 200° F.....	25.0	366		
Whisky distilling: spent mash, thick.....	56	270		
Paper industry: Sulphite paper stock (0.02 gal. per liter free Cl and 0.15 gal. per liter HCl)	120	886	0.07	86 <sup>a</sup>
Liquid fatty acids, oleic and stearic, in still....	77	3,958	6.6	

<sup>a</sup> Phosphor bronze.

<sup>b</sup> "Acid-resisting" bronze.

ments, to as little as one-fifteenth in others, of that of plain iron. Its corrosion resistance in most media is not much inferior to that of ordinary foundry bronzes and in many is superior to it.

The petroleum-refining industry was the earliest user of this material and makes wide use of it today for pumps and compressors, for valves and fittings handling acid sludges, caustic alkalis and distillate, etc. In these applications it has principally replaced plain iron, which it outlasts from three to five times.

Its use has subsequently extended to the chemical and allied industries—pulp and paper, soap manufacture, sewage disposal—where it has

replaced plain iron and often other materials as well for pumps, valves, fittings, stills, etc. This material has even invaded the household in the form of the kitchen skillet!

Although definitely inferior in corrosion resistance to the austenitic "stainless" steels, particularly when "stainlessness" or complete freedom from rusting is required, this type of iron has rapidly gained popularity for applications requiring at moderate cost a machinable, corrosion-resistant casting of fair strength, moderate hardness and good wear resistance. It has usually been introduced in replacement of plain iron but sometimes has replaced bronze and even other more expensive materials.

Irons of composition similar to Ni-Resist are nonmagnetic, and together with those containing 66 per cent manganese and 10 per cent nickel and known as "No-mag" are used for electrical castings where low magnetic permeability is required as well as high electrical resistance. Incidentally, "No-mag" was probably the first austenitic cast iron commercially used.<sup>11</sup>

At about the composition of Ni-Resist, austenitic irons have a high coefficient of thermal expansion, about 50 per cent higher than that of plain iron. In consequence they have been used for aircraft-engine cylinder liners of high thermal expansion to match that of the aluminum-alloy pistons running in them. For similar reasons they are used for valve-stem guides on gasoline engines and for internal chillers in foundry molding operations.

At a higher nickel content, about that of Invar, these irons have a low coefficient of expansion and have found special applications where low thermal expansion is required; such, for example, as paper plate dies in gauges and in glass holding machinery for light bulbs.

These highly alloyed corrosion-resistant irons present an excellent illustration of the capacity of cast iron, under manipulation, to develop new and valuable resources permitting it to invade industrial fields wholly new to it.

*"Growth"-resistant Iron.*—In addition to the corrosive conditions at ordinary temperatures which iron is called upon to meet, it is widely used for castings exposed to oxidizing conditions at higher temperatures—in gas-engine or oil-engine cylinders and exhaust manifolds, for steam valves, in grate bars for the combustion of coal and for glass or metal molds. Ordinary iron has long been known to suffer impairment of strength and structure during exposure at these temperatures, associated with certain volume changes, which have earned for this phenomenon the name of "growth."

Plain gray-iron castings may thus through combined oxidation and growth increase in volume by rather enormous amounts—over 50 per cent. This instability has been disturbing to engineers and has been the reason for the replacement of iron by steel in some types of service.

It has been found possible, however, to ameliorate this disability in iron and to develop special irons which are substantially growth-free.

Without entering into an extended discussion of the phenomenon of growth, it may be said that it is known to be associated with the instability of iron carbide and with its decomposition at higher temperatures into temper carbon, as well as to the damage suffered internally in iron when it is heated and cooled through its transformation-temperature range at about 1200° F., where it contracts and expands in volume.

Growth phenomena above and below the transformation temperature are somewhat different in character but the methods which have been found effective in reducing the susceptibility of iron to growth appear in

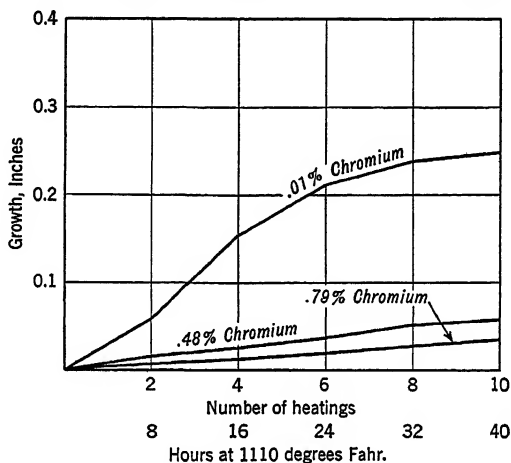


FIG. 11.—EFFECT OF CHROMIUM ON GROWTH OF CAST IRON (*Burgess, 1932*).

general to be valid in connection with both. These methods may be resolved into two groups, comprising on the one hand modifications of composition which tend to increase the structural stability of the carbides and on the other the more drastic recourse to an iron which undergoes no thermal transformation.

Ferritic or pearlitic irons can be improved in growth behavior by lowering their silicon or their carbon contents, particularly when, as in the hot-mold process, pearlitic irons, these may be lowered as far as 3 per cent of carbon and 1 per cent of silicon.

With or without such favorable adjustments of the base composition of the iron, additions of elements which induce chill and confer stability upon the carbides improve growth resistance very substantially. The element which is today most commonly used for this purpose is chromium, and whether in gray or white iron castings, growth-resistant, pearlitic alloy irons are likely to contain this element in amounts up to 1 per cent and even more. The effect of chromium in reducing growth above the critical temperature is well illustrated in the data of Fig. 11. A chro-

mium content of 0.79 per cent reduces the growth of iron to less than one-fifth of its value in plain iron. Vanadium appears also to exercise a very strong stabilizing effect upon carbides and may find increasing favor in growth-resistant pearlitic irons.

If the castings for use at high temperatures do not require machining and therefore may be of white or mottled iron, which incidentally is itself more resistant to growth than is gray iron, single additions of chill-inducing elements are likely to be used.

If, however, growth resistance is required in machinable gray castings, balanced alloy additions such as of chromium and nickel are chosen, or the chilling effect of the added chromium is offset by appropriate increase in the silicon content.

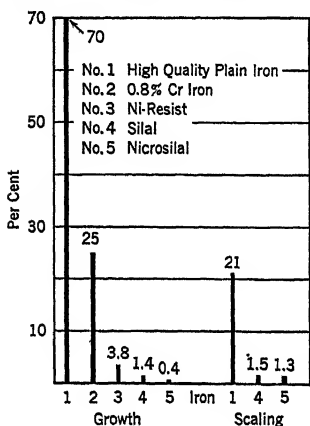


FIG. 12.—BEHAVIOR OF SEVERAL VARIETIES OF GROWTH-RESISTANT IRONS IN RESPECT OF GROWTH AND SCALING AT HIGH TEMPERATURES.

Based upon repeated heating at 1750° F. for 10 cycles, 4 hr.

All materials heated through about 10 cycles above transformation temperature under reasonably comparable test conditions.

austenitic iron such as the "Nicrosilal" developed by the British Cast Iron Research Association exhibits superior resistance to growth and to scaling at high temperatures as may be seen from Fig. 12. This iron contains 2 per cent chromium, 18 per cent nickel and 6 per cent silicon. The Ni-Resist type of austenitic alloy iron is likewise a growth-resistant and oxidation-resistant iron. Both of these compositions are substantially stable in volume and properties at temperatures up to and even above 1500° F. as may be observed from Fig. 12.

Ni-Resist has found many practical applications in replacement of plain iron and exhibits substantially superior stability at high temperatures—for example, as in glass molds and rolls, grate bars, stoker tuyeres, miscellaneous furnace parts, stove lids. Hot sections of glass annealing

All of these methods are currently practiced in improving the growth resistance of pearlitic irons and they permit restraint of growth under various conditions to as little as one-half, sometimes to one-fifth, of its extent in plain iron. The alloy irons of these types, particularly those containing amounts of chromium up to 1 per cent, show also a diminished rate of oxidation at high temperatures and scale less readily than plain irons. Such irons are widely used for grate bars, for stoker links, glass and metal molds, die-casting machine parts and melting containers.

If still greater thermal stability and oxidation resistance are required, a more highly alloyed composition of iron must be chosen, preferably one which undergoes no thermal transformation at high temperatures. An

furnaces operating at 1100° to 1400° F. have outlasted plain cast-iron parts which they have replaced as much as ten to one.

Although these irons possess excellent heat-resisting properties at moderate temperatures, they are definitely inferior to the chromium-iron and chromium-nickel iron alloys and are not recommended for service at temperatures over about 1500° F.

Ferritic irons containing 5 to 7 per cent aluminum, as well as 6 to 7 per cent silicon (Silal) have also been used for growth and heat-resistant castings and likewise exhibit excellent performance in this sense. They are somewhat more fragile than the austenic iron, however.

Reference should be made also to the high-chromium, high-carbon alloys containing from 15 to 30 per cent chromium and from 1 to 2.5 per cent carbon. These alloys have also very superior heat-resisting properties and resistance to oxidation.

#### HIGH-STRENGTH PEARLITIC MALLEABLE IRON

It is not possible for me to extend my remarks much beyond the field of gray and chilled iron. I do want, however, to say a general word about a direction of metallurgical development in malleable iron, which is, in my opinion, of considerable significance—that of so-called pearlitic malleable iron.

If the graphitizing heat-treatment for conventional malleablizing is interrupted before complete graphitization, a material is secured of substantially pearlitic matrix together with temper carbon. The same structural result may be attained by reheating completely graphitized and ferritic malleable above its transformation temperature for partial reabsorption of temper carbon into solid solution.

The resulting material possesses greater hardness and higher strength than the usual ferritic malleable, at the sacrifice of some ductility. Tensile strength values of over 75,000 lb. per sq. in. and as high as 100,000 lb. per sq. in. are currently obtained, as compared with 50,000 lb. per sq. in. for ferritic malleable.

These are values comparable with those of medium grades of cast steel, and while the ductility of these malleable irons is much less than that of steel—from 3 to 10 per cent elongation in the tensile test—they have nevertheless a considerable ability to withstand overstrain and overstress. Pearlitic malleable of the several varieties produced have found considerable application, particularly for castings requiring greater wear resistance—such, for example, as in chain products, bearings and brake drums—than is offered by ordinary malleable.

Alloy additions are frequently made to pearlitic malleable irons both for the purpose of improving the structure and properties, and in order to control or retard graphitization—the most common alloys for this

purpose being manganese, molybdenum, copper, nickel and, in small amounts, chromium.

These pearlitic malleable irons are interesting both from the metallurgical and the engineering standpoints as constituting an important step in bridging the gap between cheap but brittle iron and ductile but more expensive steel. With respect to physical properties, they represent a compromise between the two which not only proved useful industrially but has challenged our imagination to further steps in the same direction.

And those further steps have not been lacking! In the search for a material which will best and most economically meet the complex requirements of a high-speed gasoline motor crankshaft, the Ford Motor Co. has developed a copper-chromium-carbon alloy, which chemically and structurally lies between steel and pearlitic malleable and could without too much stretching of the meaning of these terms be regarded as a derivative of either. Whatever be its proper genetic name, its good engineering properties and its economy of fabrication have permitted it to become the first "ironlike" material used for passenger-car engine crankshafts and it has deservedly been stimulating to engineering and to metallurgical thought during the past year or so since it was adopted for this use.

It must impress us all alike that invention of this sort, breaking through the bounds of our conventional conception of materials, may be expected to bring in its train other similar and equally useful developments and should, when practiced in the "no-man's" land bordering cast iron, serve to extend still further the limits of usefulness of this material. Such developments tempt us to hope that we may sometime even attain that ideal objective—ductile gray iron!

### CONCLUSION

Much more could be said about the characteristics and uses of modern iron, but, my watch warns me of the desirability of bringing to a close this, I fear, rather sketchy picture of the response of iron and of iron foundries to the demands of modern industry.

Along with the many improvements which have featured this response has come something else as well—a progressive realization that the behavior of gray iron under the stresses imposed upon it in service is much better than would be inferred from its behavior in the conventional tensile test. And stimulated undoubtedly by the success of the cast-iron crankshaft, the viewpoint is gaining ground among engineers that the principal disability of iron—its low ductility—has been more widely advertised by this test than it deserves.

Graphite flakes in iron restrict and localize plastic deformation in it to those small blocks or cells of ductile matrix material bounded by the flakes. In consequence iron cannot be grossly deformed or distorted, as can steel. But it does not follow, as we have perhaps carelessly inferred,

that iron cannot accommodate itself to those smaller plastic movements which are required of a machine part in order to permit it to absorb safely these temporary overstresses which are actually encountered in service.

Many metal parts—for example, a threaded screw—have sharp changes in contour, which may almost as effectively restrict the possibility of deformation under overstress as do the graphite flakes in iron. At such “notches” steel cannot utilize its superior capacity for gross deformation and may have to behave much like iron! A sharply notched tensile-test specimen may in ductile steel not display much more gross ductility than in iron.

When we examine the capacity of iron to withstand repeated over-stresses of the magnitude actually encountered in service, and when local stress concentration at notchlike contours is involved, we find a very interesting picture. Thum<sup>12</sup> quotes the results of fatigue torsion and bending tests on steel and iron crankshafts (which, of course, have sharp changes in section and contour). Crankshafts of high-grade steel, of tensile strength ranging from 100,000 to 200,000 lb. per sq. in. failed at much lower applied loads—from 10,000 to 15,000 lb. per sq. in.—and in consequence of local stress concentration. Similar shafts of high-test iron of about 50,000 lb. per sq. in. tensile strength, failed at loads only about 25 per cent less, although the tensile-test strength of this iron was from 50 to 75 per cent less than that of the steels! In another series of tests made in this country\* high-strength alloy-iron crankshafts tested in fatigue with the center bearing offset  $\frac{1}{32}$  in., showed a life of 80 hr. as compared with 16 hr. for similar crankshafts in steel.

Cast iron of good quality is evidently not far inferior, and may be sometimes even superior, to steel in what has been called “design strength” or “form strength”; namely, in capacity to withstand applied loads and repeated moderate overloads when applied to service parts of usual complexity of shape and contour which induce local stress concentration.

It is well recognized that gray iron is superior to steel in its capacity to absorb vibrational energy safely. Its damping capacity is substantially higher than that of steel and may be double or tenfold that of steels of high elastic limit. This, curiously enough, is largely in consequence of the effect of those structural features of cast iron which impair its gross ductility and which alter the character of its elasticity. This higher damping capacity permits iron to “cushion” the effects of “whipping” and vibration in machine parts, which if undamped would not only impair the proper functioning of the machine but would lead ultimately to fatigue failure.

These recent, scientific findings of investigators only confirm the practical fact long known to users of it that cast iron will stand much abuse!

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\* Private communication.



And so when we consider the low cost of iron; when we consider those characteristics of iron for which it has always enjoyed respect—the ease and economy of its fabrication into complex shapes and forms and its excellent frictional properties and resistance to wear; and when finally we appreciate, as I have attempted to show, how the useful range of its properties has in recent years been extended and how iron has been more flexibly adapted to a wide variety of industrial service, I think we may agree that the renaissance of cast iron which we have witnessed in the last 15 years is likely to continue and to gain momentum as the years pass by.

In connection with the presentation of this lecture I have been privileged to receive many private communications and data concerning several of its aspects and I wish to express my grateful appreciation to all of those who have rendered such friendly assistance.

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## Offsetting Increased Labor Cost in Southern Blast-furnace Operation

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(Cleveland Meeting, October, 1936)

NOWHERE can there be found a more misleading statement than the old one that "Iron can be manufactured cheaper in the South." During the past decade ironmakers and users of iron have heard varied and sundry stories of the wonderful resources of the Birmingham district, including abundant ore and coal fields, cheap labor, a wonderful climate and similar industrial Utopian statements. Birmingham represents the major portion of the iron business in the South, and as Birmingham fares so goes the iron business of the South.

The intent of this paper is to shed some light on the actual conditions surrounding ironmaking in the South, especially in the Birmingham, or North Alabama, district. By a presentation of facts it is desired to point out that the "cheap iron" of the industrial South is a thing of the past, primarily because of increased labor cost and because labor is radically different in performance to what it was years ago. Also, because most of the raw materials needed in ironmaking that would be classed better than inferior are gone.

### IMPORTANT FACTORS

The several important factors that have been responsible for this change are:

1. Shrinkage of the iron business in the South.
2. Increased labor cost.
3. The development of the South, with an industrial trend, without a substantial increase of its own iron-consuming market.
4. Increased freight rates, which has narrowed the market that might be reached from this district.
5. Depletion of the better grades of raw materials, both ore and coal.

*Shrinkage of Iron Business in South.*—Table 1 was prepared in early 1936 and revised in 1937, of blast-furnace units in the North Alabama district, considering the year 1936 compared with a maximum number of furnace units of previous years, the peak point being very near the year

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1917. This comparison indicates that the shrinkage of the iron business in the North Alabama territory is primarily due to increased labor cost and narrowing of the shipping market.

During the year 1917 there were 38 operating blast furnaces in the North Alabama district out of a total of 47, while during 1936 only 15 of 22 available blast furnaces were operated. In other words, the number

TABLE 1.—*Shrinkage of Pig Iron, Ore, Coal and Coke Business in Alabama*  
(From maximum number of operating units as compared with units operating or available in 1936)

Operations	1936	Maximum <sup>a</sup>	Sources of Data
<b>Blast furnaces:</b>			
Operating.....	15 { 12 entire year, 3 part time	38	American Iron & Steel Institute, Annual Report.
Total stacks.....	22 <sup>b</sup>	47	
Tons produced.....	1,993,679	2,953,705	Estimated—directly and indirectly employed.
Men worked.....	15,557	23,610	
<b>Coal mines:</b>			
Operating.....	229 { 79 R.R. connection, 150 wagon	301 <sup>c</sup>	Alabama State Mine Inspector's Office.
Tons produced.....	12,698,749	21,508,812 <sup>d</sup>	
Men worked.....	23,297 (3.01 days part time)	27,648	
<b>Iron-ore mines:</b>			
Operating.....	28 <sup>d,e</sup>	42 <sup>d</sup>	U. S. Bureau of Mines.
Tons produced.....	3,240,000 <sup>d,e</sup>	7,037,707 <sup>d</sup>	
Men worked.....	3,998 <sup>d,e</sup> (part time)	8,689 <sup>d</sup>	
<b>Coke ovens:</b>			
Operating.....	940	8,115 <sup>e</sup>	{ 1936: Ala. State Mine Inspector's office. Maximum: U. S. Bureau of Mines.
Tons coke produced	3,082,459	4,868,598	
Men worked.....	876	3,720	{ 1936: Estimated directly and indirectly employed. Maximum: U. S. Bureau of Mines.

<sup>a</sup> All maximums shown are for year 1917 unless otherwise noted.

<sup>b</sup> Two of these being dismantled.

<sup>c</sup> Includes beehive ovens.

<sup>d</sup> Includes major brown-ore operations.

<sup>e</sup> Year 1920.

<sup>f</sup> Year 1926.

<sup>g</sup> Year 1935.

of available units has shrunk from 47 to 22, or 53 per cent in 19 years, crudely indicating the shrinkage of the iron business in the South. Of course, several of the blast furnaces have been enlarged and tonnage per furnace is considerably higher than in 1917, but total capacity for producing iron tonnage in 1936 is only 62 per cent of what it was in 1917.

*Increased Labor Cost.*—Labor has had a great deal to do with this shrinkage because increased labor rates have caused the proportion of labor in total cost to increase substantially. Current authentic data on

this subject are given by taking Government figures and comparing rates and labor cost. Table 2 is a statement prepared of 1000 wage rates in the Southern blast-furnace industry and compares the years 1933 and 1935—a pre-N.I.R.A. period with a post-New Deal period. It may be noted from this tabulation that prior to the N.I.R.A. approximately 40 per cent of all workers in the blast-furnace industry were paid wages

TABLE 2.—*One Thousand Wage Rates of Workmen in Blast Furnaces, Southern District<sup>a</sup>*

Year	1933			1935		
	Number of Men	Per Cent	Cumulative Per Cent	Number of Men	Per Cent	Cumulative Per Cent
Average Hourly Rate						
\$0.15 -0.20.....	151	13.7	13.7			
0.20 -0.225.....	110	9.9	23.6			
0.225-0.25.....	66	6.0	29.6			
0.25 -0.275.....	33	3.0	32.6			
0.27 -0.30.....	85	7.7	40.3	1	0.1	0.1
0.30 -0.325.....	51	4.6	44.9	124	11.9	12.0
0.325-0.35.....	47	4.2	49.1	94	9.1	21.1
0.35 -0.375.....	56	5.0	54.1	73	7.1	28.2
0.375-0.40.....	57	5.1	59.2	60	5.8	34.0
0.40 -0.425.....	75	6.8	66.0	60	5.8	39.8
0.425-0.45.....	39	3.5	69.5	62	6.0	45.8
0.45-0.475.....	34	3.1	72.6	43	4.2	50.0
0.475-0.50.....	72	6.5	79.1	36	3.5	53.5
0.50 -0.55.....	98	8.8	87.9	96	9.3	62.8
0.55 -0.60.....	43	3.9	91.8	60	5.8	68.6
0.60 -0.65.....	39	3.5	95.3	95	9.2	77.8
0.65 -0.70.....	27	2.4	97.7	81	7.8	85.6
0.70 -0.75.....	16	1.4	99.1	45	4.4	90.0
0.75 -0.80.....	2	0.2	99.3	31	3.0	93.0
0.80 -0.90.....	6	0.5	99.6	45	4.4	97.4
0.90 and over.....	2	0.2	100.0	27	2.6	100.0
Total.....	1109	100.0	100.0	1033	100.0	100.0

<sup>a</sup> From Bureau of Labor Statistics, Serial R-380 (1936).

less than 30¢ per hour, while in 1935, 40 per cent of all blast-furnace workers earned as much as 45¢, or an increase of 50 per cent.

It might be easily proved, from specific company records, that cost of labor in pig iron in the Birmingham district has advanced from 57.69 to 72.22 per cent in the total cost since 1932. Coal-mining labor, which ultimately gets into pig-iron cost, has increased 88 per cent since 1932; while raw materials other than labor have advanced only 14.46 per cent. This unbalanced labor to material advance is definitely shrinking the iron business in the Birmingham district because increased cost continues to

narrow the radius of the shipping range, which already has shortened several hundred miles, and the remaining area does not furnish a market equal to the capacity to produce.

Extensive mechanization has played an important part in offsetting this increased labor cost, as is shown by Fig. 1, which shows pig-iron cost after 18 years virtually the same. Individual rates have increased by groups, as shown by Table 3, in which the hourly wage rates of 1933 are compared with those of 1935 for the several occupations of a blast-furnace operation, indicating an increase ranging from 10 to 15 per cent.

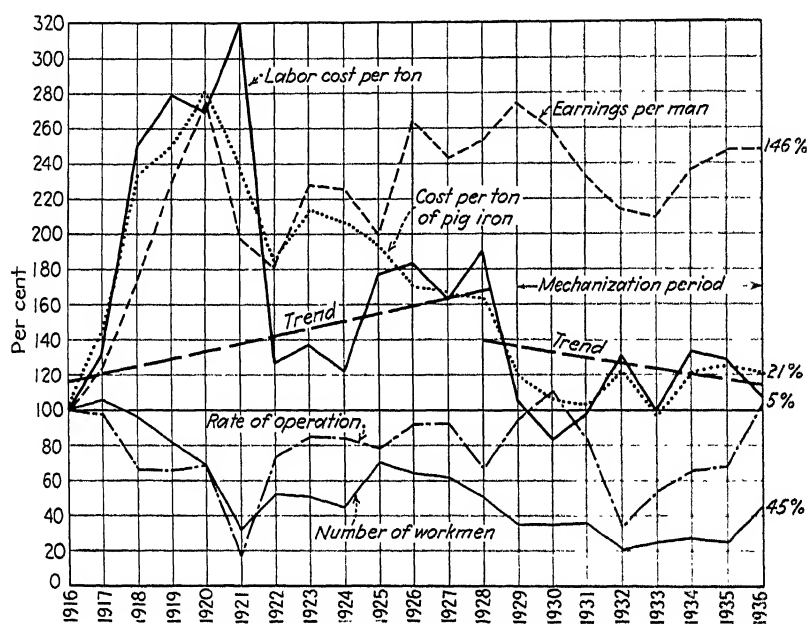


FIG. 1.—VARIATIONS IN COST OF LABOR.

Fig. 1 is a graphic chart of a single large operator in the Birmingham district that employs approximately 2000 men in the merchant iron business, including labor in ore and coal mining. Taking records over a period of 16 years of this particular company and computing them in percentages, a definite trend of increased labor cost is evident. This graph shows that total cost per ton of pig iron approximates within 21 per cent of the men employed in 1916. On the other hand, it pays this 55 per cent of its former men 246 per cent of the wage per man per annum that it paid in 1916. The producing rate of this company is within 5 per cent of what it was in 1916. An interesting feature of this chart is the downward trend of the number of workmen and a definite upward trend of wages paid per man; while the trend of the cost per ton of iron is almost level and definite proof that many creditable things have been

TABLE 3.—Average Hourly Rates for Blast-furnace Employees, Southern District<sup>a</sup>

Year	1933		1935	
Occupation	Number of Men	Average Hourly Rate	Number of Men	Average Hourly Rate
Stock-house men.....	26	\$0.329	40	\$0.461
Larrymen or scale-car men.....	20	0.30	28	0.423
Skip operators.....	25	0.348	31	0.444
Blowers.....	20	0.67	23	0.881
Stove tenders.....	20	0.410	30	0.565
Blowing engineers.....	28	0.462	21	0.678
Keepers.....	30	0.349	30	0.493
Keeper helpers.....	50	0.301	63	0.412
Pig-machine men.....	47	0.367	38	0.455
Miscellaneous service.....	64	0.346	92	0.50
Common labor.....	127	0.202	150	0.326
Supervisors.....	55	0.516	43	0.746
Indirect labor.....	156	0.362	103	0.569
Total and average.....	668	\$0.382	692	\$0.534

<sup>a</sup> From Bureau of Labor Statistics, Serial R-380 (1936).

done to equalize cost. An attempt to explain some of the more meritorious items that have brought about this particular picture comprises a major portion of this paper.

A recent report of the Southern States Industrial Council on comparative wage rates of the North and South was recently issued in a bulletin which shows that since February 1933 wage rates have advanced 30.4 per cent in the South and 14.7 per cent in the North. The average hourly rates in the South were 31.6¢ per hour in 1933 and have increased to 41.2¢ in 1936, while in the North the hourly wage rates were 47.5¢ in 1930 and are now 54.4¢. This particular study includes all Southern industries and is not specifically tied into blast-furnace operations. However, it does indicate that in actual money the Southern hourly wage has advanced 9.6¢ as against 6.9¢ in the North, or a net gain in the South of 2.7¢ per hour, which, of course, is applicable to the blast-furnace business. The Southern rates, beginning at a lower level than the Northern, the 2.7¢ per hour gain in the South is a larger percentage than the gain in the North, thus lessening the much talked of differential.

*Wage Differential.*—For years the impression has prevailed that there is a wage differential between the industrial North and the industrial South. This is true; and there should exist a wage differential because of the very simple fact that owing to a very limited local market for the Southern industries, a wage differential must exist; for because of that

limited local market, the Southern manufacturer is forced to ship long distances and to absorb a substantial portion of the freight cost in his operating cost.

The wage differential, however, during the N.I.R.A. period was radically reduced, particularly in the iron and steel business in the Birmingham

TABLE 4.—*Average Weekly Earnings of Wage Earners in Blast Furnaces in 1935*

Occupation	Eastern District		Pittsburgh District		Great Lakes and Middle West District		Southern District	
	Number of Wage Earners	Average Weekly Earnings	Number of Wage Earners	Average Weekly Earnings	Number of Wage Earners	Average Weekly Earnings	Number of Wage Earners	Average Weekly Earnings
Ore-bridge operators.....	30	\$26.87	23	\$26.24	44	\$24.47	<sup>a</sup>	<sup>a</sup>
Transfer-car operators...	21	18.37	<sup>a</sup>	<sup>a</sup>	38	20.84	<sup>a</sup>	<sup>a</sup>
Stockers.....	90	13.83	183	15.45	143	19.42	40	\$17.59
Larrymen.....	23	20.24	74	21.34	103	22.73	28	15.97
Larrymen's helpers.....	<sup>a</sup>	<sup>a</sup>	20	19.18	48	18.52	<sup>a</sup>	<sup>a</sup>
Skip operators.....	<sup>a</sup>	<sup>a</sup>	63	20.99	42	22.49	31	16.03
Blowers.....	15	39.63	35	38.56	71	46.01	23	43.19
Stove tenders.....	28	18.87	62	21.96	65	22.68	30	21.70
Blowing engineers.....	<sup>a</sup>	<sup>a</sup>	43	27.34	57	27.64	21	26.60
Blowing engineers' assistants.....	<sup>a</sup>	<sup>a</sup>	43	22.46	40	24.61	<sup>a</sup>	<sup>a</sup>
Keepers.....	27	19.50	72	22.72	73	23.13	30	18.26
Keepers' helpers.....	84	16.88	201	18.87	210	20.13	63	15.41
Pig-machine men.....	35	16.77	90	13.81	112	21.23	38	16.94
Cindermen (at dump)...	<sup>a</sup>	<sup>a</sup>	43	16.88	42	18.64	<sup>b</sup>	<sup>b</sup>
Common laborers.....	78	14.01	140	14.89	178	18.12	150	10.53
Miscellaneous labor.....	67	18.10	74	16.74	90	18.53	92	19.08
Clerical, plant.....	<sup>a</sup>	<sup>a</sup>	40	23.06	35	24.24	<sup>a</sup>	<sup>a</sup>
Supervisory, plant.....	56	32.92	156	38.25	168	33.08	43	32.69
Other direct labor.....	<sup>a</sup>	<sup>a</sup>	39	24.70	29	24.31	<sup>a</sup>	<sup>a</sup>
Other indirect labor.....	62	20.47	228	21.74	163	22.54	103	22.01
Average of totals.....	616	21.27	1629	22.38	1751	23.67	642	21.23

<sup>a</sup> Not a sufficient number reported to present averages.

<sup>b</sup> None reported.

district. Base labor rates, prior to the N.I.R.A. approximating 18 to 20¢ per hour, were increased to a 30¢ minimum at the beginning of the Codes. This was a blanket 50 per cent increase. It is difficult to explain to the Northerner how 18 to 20¢ per hour could be a fair hourly wage, because it is impossible to depict living conditions, cost of food-stuff, and year-around cost of clothing. One must visit the site and see the several favorable factors that enter into living in the South that

allow an individual to live happily on a much smaller wage than he would be able to do in the North. It is the writer's opinion, formulated by actual contact, that the common wage earner in the South at 20¢ per hour fares considerably better and is generally happier than his brother laborer who lives in the Northern industrial centers and earns a much higher wage.

To show a comparison of average weekly earnings of blast-furnace employees by the several iron-manufacturing districts of the United States, Table 4 is taken from statistics published by the Bureau of Labor Statistics. This table shows that the stockers, or stock-house crew, of the South earn more per week than the Eastern, or Pittsburgh district, and are excelled only by the Great Lakes district. Weekly earnings of the blowing engineers, keepers, pig-machine men, cinder men and men of the supervisory force are comparable and well in line with earnings in the other districts. If these figures are representative, and undoubtedly they are because of their source, where is there such an immense differential as we hear so much of? Certainly this differential does not exist in the blast-furnace operation or the iron business in the South; in spite of the fact that everyone who knows will admit that an individual workman can live more cheaply in the South than he can in any of the other mentioned districts.

The point that is being made is the fact that in previous years a substantial wage differential did exist. Table 4 is positive proof that, as far as blast furnaces are concerned, the differential has dissipated practically to the vanishing point. The extent of the handicap placed on Southern iron manufacturers by this condition is cited by Table 1 of this paper, showing the shrinkage of the iron business in the South. These two tables are self-explanatory and need no further comment.

*Southern Raw Materials.*—For years much has been said about the wonderful resources of the Birmingham district, of the great mountain of red ore in the South and the great mountain of wonderful coal in the North; with abundant limestone and dolomite in the valley between coal and ore deposits. Table 5 is an analysis of the several seams of coal in the State of Alabama. Attention is directed particularly to the column showing ash percentage, with particular reference to the major seams of coking coal; namely, Pratt, Mary Lee and New Castle, that will average better than 10 per cent ash. Consider only the coals usable for metallurgical purposes. It is necessary to utilize extensive coal-preparation and washery plants, the average of which would represent an investment in excess of \$100,000, for a tonnage necessary to operate a single blast furnace. In other words, this coal must be washed and literally scrubbed to remove impurities to make it fit for coking purposes, and even then yields a coke ash approximating 12 to 13 per cent, or 30 per cent higher than typical Northern coke.



Attention is also directed to the percentage of sulphur. The average sulphur content of the coking coal is more than 1 per cent, Mary Lee or Big Seam coal being 1.10 per cent, Pratt, considered a low-ash coking coal, 1.57 per cent sulphur, and New Castle 2.00 per cent. Note also

TABLE 5.—Average Analysis of Alabama Coal Seams as Sampled and Analyzed on As-received Basis

Seam	Moisture, Per Cent	Volatile Matter, Per Cent	Fixed Carbon, Per Cent	Ash, Per Cent	Sulphur, Per Cent	B.t.u.
America.....	2.61	29.56	59.27	8.55	1.76	13,591
Black Creek.....	3.41	33.39	59.71	3.41	1.02	14,237
Black Shale.....	4.60	35.10	57.90	2.40	0.60	14,210
Blue Creek.....	3.84	23.64	63.01	9.48	0.70	13,478
Bragg.....	2.30	33.60	57.40	6.70	1.50	13,860
Brookwood.....	3.58	28.74	57.89	9.74	1.00	13,270
Carter.....	2.80	30.00	59.33	7.86	0.90	13,699
Clark.....	2.31	35.26	54.96	7.46	0.64	13,750
Corona.....	2.44	38.91	48.95	9.70	2.25	12,878
Gholson.....	3.01	35.17	53.34	3.47	0.67	14,232
Glass.....	2.50	31.00	54.60	11.90	0.70	13,030
Gould.....	2.97	30.21	58.97	7.85	1.83	13,622
Harkness.....	2.33	32.90	54.67	10.09	2.00	13,319
Helena.....	3.71	33.53	54.36	8.38	0.59	13,255
Henry Ellen.....	2.52	33.13	52.91	11.44	0.87	13,091
Jagger.....	2.95	29.29	52.09	15.66	0.94	12,213
Jefferson.....	2.25	32.74	58.48	6.48	3.15	13,947
Mary Lee.....	2.86	29.82	55.11	12.19	1.10	12,841
Maylene.....	2.99	36.55	53.08	7.38	0.44	13,070
Milledale.....	2.11	31.26	62.09	4.52	0.91	14,347
Montevallo.....	2.51	36.78	53.22	7.48	0.83	13,481
New Castle.....	2.97	30.46	52.82	13.75	2.00	12,593
Nunnally.....	2.22	34.41	55.37	8.00	0.95	13,566
Pratt.....	2.45	29.60	61.46	6.38	1.57	14,149
Thompson.....	3.00	35.29	54.83	6.86	0.59	13,518
Woodstock.....	3.19	34.61	58.52	3.67	1.05	14,138
Yessick.....	4.21	29.85	45.36	20.58	1.54	11,008
Youngblood.....	2.71	34.67	57.43	5.19	1.26	14,373
Mount Carmel.....	3.14	29.98	53.90	12.96	0.80	12,506

\* Reported by U. S. Bureau of Mines and taken from Forty-fourth Annual Report of State Mining Department of Alabama (1935).

the fact that there are many high-volatile coal seams in Alabama, with a noticeable absence of low-volatile coals, which are necessary sometimes for mixing with high-volatile coals to eliminate swelling during coking. Therefore it is necessary to ship low-volatile coals for mixing purposes from West Virginia or Kentucky, which adds again to production cost in the South, and is another handicap.

Table 6 gives a comparison of the several sample analyses of red ore taken a mile apart along the ore range and utilized for metallurgical purposes in the Birmingham district. By adding the silica and alumina and subtracting the lime the balance of acids and bases is shown. It is thus obvious that the coke ratio necessary to reduce these ores is considerably above that of Northern blast-furnace practice. A Northern operator would consider these ores inferior and a definite handicap to his operation. Nevertheless, they represent the best available within the Birmingham district.

TABLE 6.—*Samples of Red Ore from Birmingham District Taken about One Mile Apart*

Sample No.	Fe (Metallic Iron)	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	P
1	52.39	16.65	4.86	0.36	0.25
2	44.32	31.60		5.15	0.23
3	43.01	21.61	5.11	4.19	0.30
4	40.67	14.90		7.48	0.34
5	41.79	38.41		4.07	0.30
6	37.17	23.73	3.03	9.81	0.34
7	35.89	23.19	3.25	10.79	0.32
8	39.31	11.01		15.32	0.34
9	33.78	11.05	3.31	19.32	0.30
10	48.11	18.63	5.59	2.09	0.35

*Conclusions Regarding Increased Cost.*—The foregoing is an attempt to show: (1) that ironmaking cost in the South has increased; (2) that wages of blast-furnace employees have increased and thus have increased the cost of the iron; (3) that wages of Southern blast-furnace employees now very nearly approach wages paid in other districts; (4) that the North-South wage differential is a small margin as applied to blast furnaces; (5) that superior grades of raw materials, ore and coals are depleted and materials used now are decidedly inferior because of impurities.

The Southern iron manufacturer, therefore, has faced a tremendous problem of offsetting these items. Had they been ignored it would have banished the iron business entirely from the South. Fortunately, the Southern operator has gone to work. Apparently he has used every possible facility available to improve cost; to offset the tremendous increase in labor cost. Imagine the plight of any business, already shrinking, suddenly having its base labor cost increased 50 per cent, as happened in the South with the inauguration of the Codes, and being forced to grope blindly for quick improvements while awaiting price advances and increased volume of business.

Some of the things done in the South to offset increased cost may seem elementary to one fortunate enough to have already installed similar improvements or able to do so at once. To effect them under difficulties, however, deserves commendation; and is reason for their mention and description herein.

#### IMPROVEMENTS TO OFFSET INCREASED COST

The chart in Fig. 1 may be taken as a cross section of the iron business of the South, because it was prepared from actual records of one of the larger iron manufacturers. It shows labor cost per ton only 5 per cent increased, while earnings per man increased 246 per cent and there were employed only 45 per cent as many men as during 1916. Tonnage production being only 5 per cent in favor of 1936, the comparison is fairly considered. It is obvious that many changes in methods of operation must have been made during the intervening years. Extensive laborsaving devices must have been employed to reduce men 55 per cent. Certainly efficiency of mechanisms used has improved to hold cost within 5 per cent of the 1916 figure, if workmen earned 246 per cent more.

Many of the accomplishments or improvements from 1930 to 1935, most of which were stimulated or inspired by the necessity of cost reduction, were very ably described by Francis H. Crockard.<sup>1</sup>

#### *Sintering Flue Dust*

One of the most outstanding improvements in the blast-furnace operations in the South, and a major factor in offsetting increased labor cost, has been made at the Thomas Works of Republic Steel Corporation, where a complete sintering plant was installed during the first part of 1936 and put into operation in June. This unit is the first and only sintering operation in connection with blast furnaces in the Southland. This statement will be difficult for the Northern blast-furnace operator to understand because there are many sintering plants in the North and practically all the blast furnaces use a great deal of flue-dust sinter.

It was generally thought that it was impossible to properly sinter Southern flue dust, primarily because Southern ores are silicious and use considerably more coke than Northern blast furnaces. The dust, therefore, contains an excess of carbon. Another factor is that some of the ores used in this district are self-fluxing or more than self-fluxing and contain excess amounts of lime. Numerous experiments approaching sintering were undertaken, most of which were efforts to nodulate flue dust so that it could be charged back into the blast furnaces.

Several papers have been written on efforts to beneficiate flue dust and on treatment of dust preparatory to sintering. A Bureau of Mines

<sup>1</sup> F. H. Crockard: Five Years of Progress in Southern Blast-furnace Practice. *Trans. A.I.M.E.* (1936) **120**, 36.

publication<sup>2</sup> stated as a conclusion: "The high content of gangue in the average flue dust of the Birmingham district makes it unfit to treat in the same manner as those of other districts where direct sintering is sufficient to produce a satisfactory product."

One local scientist spent considerable effort in separating the coke, or carbon, out of flue dust by a jig and then briquetted the remaining material for recharging into the furnace. His results were satisfactory but the expense connected with the process was prohibitive.

Early in 1935, Republic Steel officials became interested in sintering Southern flue dust, because great mountains of flue dust were available at the blast-furnace plant, the material having been considered waste as far as Southern blast furnaces were concerned.

By a series of tests, it was found that much of the flue dust contained more than 10 per cent carbon and in most samples the carbon content ranged from 15 to 19 per cent, so that when sintered it became a molten, metallic mass. It was found, by experimentation, that dilution of this carbon with a material that contained no carbon made it sinter readily. Extensive tests were subsequently run on a Dwight-Lloyd sintering machine owned by the Ducktown Chemical & Iron Co., at Ducktown, Tenn., and later at the sintering plant of the American Ore Reclamation Co., Buffalo, N. Y. These tests were run by mixing several grades of Southern flue dust with ore dust in varying proportions, and carefully noting the analyses of the resulting sinter.

Table 7 shows the percentage of ore mixed with the flue dust and resultant sinter analyses of nine of these tests; also, analyses of the ores that were mixed with the flue dust, average analysis of sludge and dump-pile flue dust. These tests show that a comparatively good grade of sinter was made by mixing 50 per cent flue dust and 50 per cent of B ore, which was over self-fluxing, containing 19.32 per cent CaO. Flue dust of No. 1 sample resulted in 14.29 per cent CaO versus approximately 20 per cent acids in the sinter. The test proved conclusively that the problem was of no importance, because it was simply a matter of diluting the carbon to approximately 8 per cent, or a point at which it would sinter.

Another mixture that was deemed acceptable, and one with which it would be possible to utilize both A and B ores, which is desirable, was sample No. 4, wherein 18 per cent of an ore that was not self-fluxing, marked A, was used and 32 per cent of an over self-fluxing ore, marked B, was used. These two ores represent the extremities of the ore range at Birmingham. A ore is taken from a mine at the northeastern extremity of the active ore field and B ore from the field at the southwestern extremity of the ore range. While all Red Mountain hard ore comes from the same seam, there is an appreciable difference in the ore from the

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<sup>2</sup> Magnetic Concentration of Flue Dust of the Birmingham District. U. S. Bur. Mines *R.I.* 2761 (1926).

several different mines on the mountain. The analyses of the two ores (Table 7) show the wide difference in acids and lime content. Mixing these two ores was desirable from Republic Steel's standpoint because it operated mines at the two extremities of the ore range.

TABLE 7.—*Test of Sintering Flue Dust Mixed with Ore, to Dilute the Carbon*  
JUNE, 1935

Mixture, Per Cent					Sinter Analyses, Per Cent					
Sample No.	Flue Dust	Sludge Flue Dust	Ore A	Ore B	Fe	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	P	Mn
1	42.0	8.0		50.0	40.93	16.68	4.81	14.29	0.30	0.59
2	42.0	8.0	18.0	32.0	40.62	18.76	4.65	13.77	0.33	0.57
3	50.0	10.0	15.0	25.0	40.83	20.08	4.88	12.19	0.26	0.62
4	40.0	10.0	18.0	32.0	40.62	23.64	5.15	12.92	0.32	0.59
5	50.0			50.0	41.14	16.24	5.07	15.51	0.36	0.63
6	50.0		18.0	32.0	40.72	18.46		12.93	0.32	0.60
7	60.0		15.0	25.0	40.72	19.32		13.14	0.32	0.66
8	50.0		50.0		40.62	17.54		10.48	0.26	0.61
9	46.0	8.0	16.0	30.0	40.62	21.98		12.08	0.31	0.65

ANALYSES OF MATERIALS USED, PER CENT

	Fe	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	P	Mn	MgO	C	CO <sub>2</sub>
Ore A.....	35.89	23.19	3.25	10.79	0.32	0.16	0.70		
Ore B.....	33.78	11.05	3.31	19.32	0.30	0.16	0.70		
Flue dust, average	34.54	16.89	3.76	8.35	0.24	0.61		10.67	6.73
Sludge, average...	33.56	16.48	4.14	10.05	0.27	0.73		13.10	4.40

The plant erected at the Thomas Works consists of arrangements for properly mixing four kinds of ore or flue-dust material. Each of the bins for the four raw materials has separate feeder tables that may be adjusted to mix the desired percentages, from which the material goes into a crusher where congealed lumps of flue dust or coke, such as are found in the old piles of flue dust, are broken down. (Fig. 2.)

The ore mixed with the flue dust is a minus  $\frac{1}{4}$ -in. hard red ore material from either of two mines and pyrites that might be purchased throughout the South from the several chemical plants or fertilizer operations. The pyrites are low in phosphorus and are used as a medium of phosphorus control.

Fig. 3 shows an arrangement of the ore screens erected at the mines to provide the minus  $\frac{1}{4}$ -in. material. There is a primary and a secondary crusher. The primary crusher is set to break the hard ore down to less than 4 in. and the secondary crusher can be set to crush the 4-in. lumps of ore down to  $\frac{3}{4}$  in., but more generally is operated at 1 or  $1\frac{1}{8}$  in. setting. The ore then is put over a large 60 by 144-in., heavy-duty, double-deck,

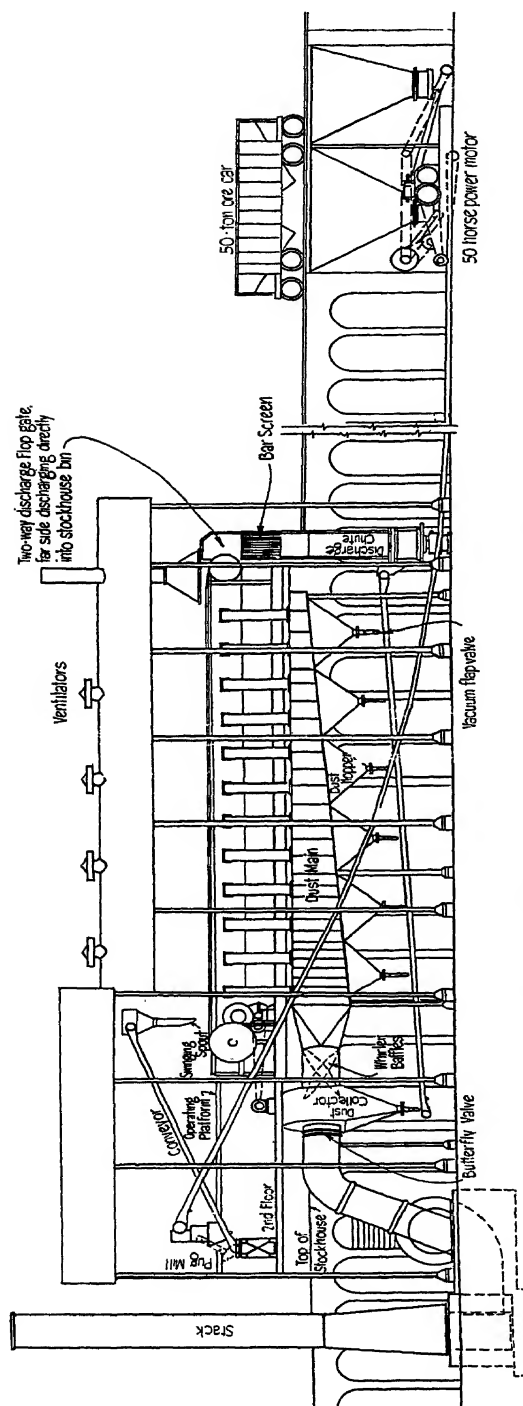


FIG. 2.—GENERAL ARRANGEMENT OF SINTERING PLANT AT THE THOMAS BLAST-FURNACE WORKS.  
(Reproduced by permission, from *Steel*, Feb. 8, 1937.)

shaker screen of the Robins Gyrex type. This screen has a mesh of 1-in. clear opening on the top deck and  $\frac{1}{4}$ -in. clear opening on the bottom deck; thus providing a plus 1-in. material, which goes over the top; an intermediate of minus 1 plus  $\frac{1}{4}$ -in., and a fine ore going through the  $\frac{1}{4}$ -in. clear opening screen. The three sizes of ore are binned in such a manner that they may be loaded directly into railroad cars or stored so that the cars may be shifted on the tracks in proper sequence.

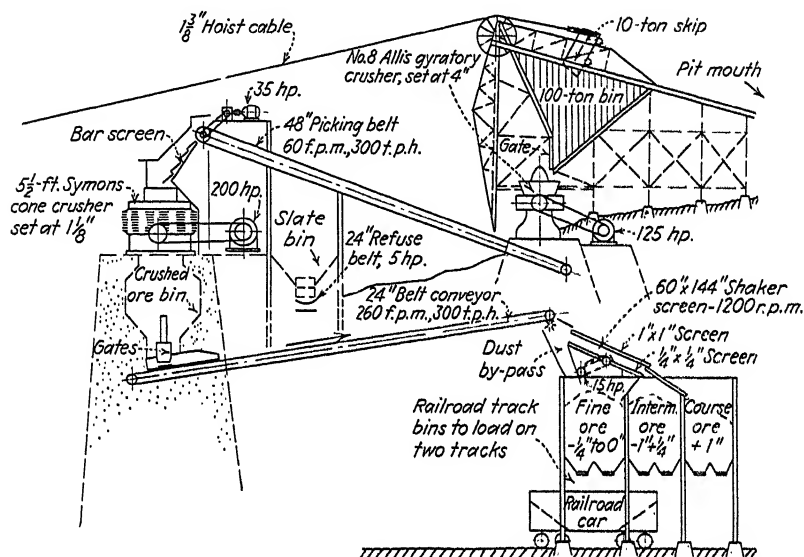


FIG. 3.—ARRANGEMENT OF ORE-PREPARATION PLANT AT RAIMUND MINE, REPUBLIC STEEL CORPORATION.

In obtaining the minus  $\frac{1}{4}$ -in. ore for sintering, there are also obtained two definite sizes of ore that might be charged directly into the blast furnace, effecting the many advantages of charging sized ores, as pointed out by C. C. Furnas and T. L. Joseph.<sup>3</sup>

Southern ores, being of hematite structure and hard, when screened as outlined above provide a wonderful material for blast furnaces, because the large sizes are as clean as if separately washed and the finer sizes are segregated and sent to the sintering plant. This ore-screen arrangement at the ore mines of Republic Steel Corporation is an outstanding improvement in the Southland. It is interesting to blast-furnace men because the complete arrangement for providing sized ore, exclusive of the crushing equipment that was already installed, represents an investment of less than \$10,000. There is no reason why any mining operation already having a primary and secondary crushing unit cannot install proper

<sup>3</sup> C. C. Furnas and T. L. Joseph: Stock Distribution and Gas-solid Contact in the Blast Furnace. U. S. Bur. Mines *Tech. Paper* 476 (1930).

screens and bins for providing sized ore at an investment of less than \$10,000 if it has means of disposing of the very fine ore, such as sintering.

The sintering plant is on the blast-furnace property. It consists of the four bins mentioned above, a heavy-duty, double-roll crusher, incline conveyor to the pug mill, or mixer, where proper moisture is added, thence to machine swinging spout, or feeder. The machine is a Dwight-Lloyd, 72 in. wide by 76 ft. 6 in. long, containing 98 pallet units and having a capacity of 60 tons of sinter per hour when operated at a speed of 112 in. per minute. This speed may seem too great to Northern operators, but it must be remembered we are dealing with flue dust containing more

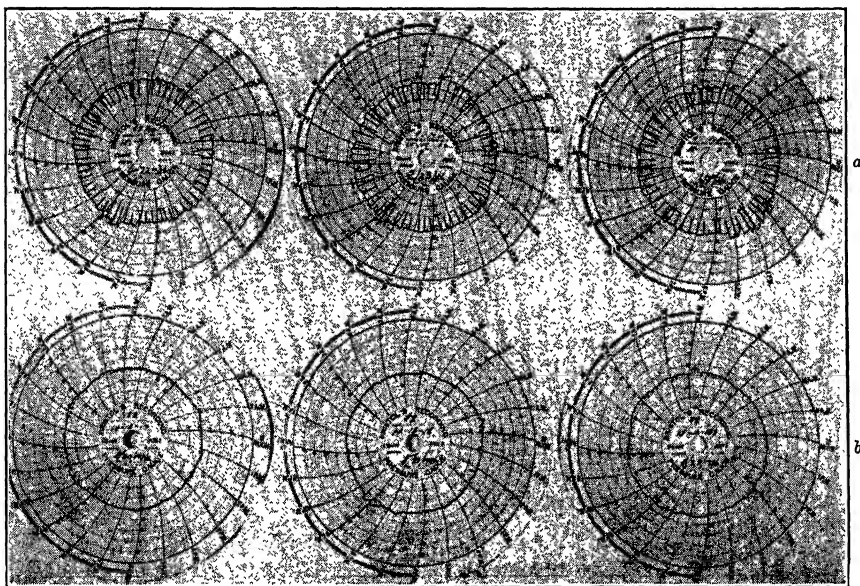


FIG. 4.—BLAST PRESSURE DURING AUGUST 1936.  
*a*, before, *b*, after using sinter, sized ore and electric automatic clay gun.

than 10 per cent carbon and sintering speed ranges from 8 to 14 in. of bed depth per minute.

A unique feature of this particular plant is that it is erected directly on top of the stock house in such a manner that the sinter from the machine may be directly discharged into the stock-house bins, thence through scale cars to skip and charged into the furnace without railroad switching or handling. By simply manipulating a gate it may be discharged into railroad cars for stocking or for other disposition.

Another feature is that this plant is open; it is not housed in with siding as is the custom in the North. This, of course, is because of the climate in northern Alabama, and affords a wonderful relief from the dust problem that ordinarily goes with a closed sintering plant.



The advantages and effects of sinter on the furnaces are shown in a crude way by Fig. 4, a record of the blast pressure of No. 2 blast furnace before and after using sinter, sized ore and installation of an electric automatic clay gun. Note that "before" it was necessary to "snort" the furnace in order to move it, while "after" the furnace moved itself, which is another novelty in Southern blast-furnace operation, because few Southern furnaces move themselves.

Sinter made from "home-grown" flue dust has been placed on the furnaces at Republic's Thomas Works in varying amounts of 20 to 50 per cent, and even 100 per cent for a few days. Its effect on the furnace, along with charging sized ores, may be seen from the following practice on one furnace, taking an equivalent period before and after using sized ore and sinter:

	Before	After
Flue dust produced, lb.....	16,067,800	13,579,100
Flue dust per ton of iron, lb.....	140	121
Charges.....	19,478	18,947
Average daily production, tons.....	451	457

There is a difference of 2,488,700 lb. of flue dust, or 15.5 per cent of the total produced in the "before" period. The charges during the "after" period were 531 less, yet the average production was greater; clearly indicating the improvement.

Installation of the sintering plant at the Thomas Works of the Republic Steel Corporation has been one of the most important steps taken in the South in offsetting increased labor cost, and undoubtedly is a feature that will be followed by other Southern blast furnaces.

### *Superock*

Another novel improvement Republic has made that is expected to decrease cost is the manufacture of Superock, which is the trade name for an inert, light-weight aggregate for concrete, insulation and masonry work (Fig. 5). It is made by pouring molten blast-furnace slag into a rotating machine, which whips and cools it and breaks up the lumps. A small amount of water is used at the entrance spout, which literally explodes the hot slag. The concussion, the rotary paddle force of the machine, and the expansion of gases released from the slag while in the machine, blows up the cooling, or hardening slag, while still plastic, into a mass of tiny cells. Each cell is separated from the others and surrounded by a thin wall of very hard and dense material. The cells have no passageways joining them nor do they connect. Under the microscope Superock is found to be a mass of these tiny air cells of varying size that cannot be seen with the eye.

While the shell of the aggregate is very hard and dense, so little of the total volume is occupied by the shell, or cell wall, that the weight is light and the large pieces are readily crushed, or broken, and screened into sizes desired. Superock thus has tensile and compressive strength approaching dump slag, yet weighs from 32 to 46 lb. per cubic foot, depending on the size, which is less than half of ordinary silicious sand aggregates. Superock mixed with Portland cement and rodded dry averages 46 lb. per cubic foot.

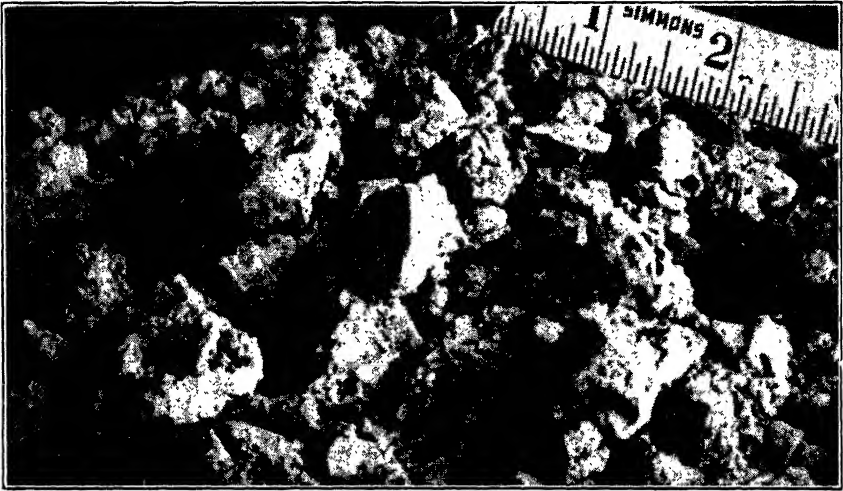


FIG. 5.—COARSE SUPEROCK, ACTUAL SIZE.

It is common knowledge that blast-furnace slag is a complex mixture of well-known rock-forming minerals. Four of the principle ones are found in Superock, as follows:

	PER CENT
Akermanite ( $2\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$ ).....	18.45
Anorthite ( $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ).....	11.97
Calcium bisilicate ( $\text{CaO} \cdot \text{SiO}_2$ ).....	34.28
Gehlenite ( $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ ).....	32.90
	<hr/>
	97.60
Calcium sulphite (1.61 per cent), manganese oxide (0.79 per cent).....	2.40
	<hr/>
	100.00

The average slag analysis used to make Superock is as follows:  $\text{SiO}_2$ , 38.0 per cent;  $\text{CaO}$ , 42.3;  $\text{Al}_2\text{O}_3$ , 15.0;  $\text{MgO}$ , 3.2;  $\text{MnO}$ , 0.5; S, 1.0; total 100.0.

Superock's thermal conductivity is 36 per cent of ordinary concrete and thus it is an ideal insulation material. Its sound-absorbing value is

15 per cent when ordinary concrete is zero. Nails may be driven into pressed blocks or walls of Superock concrete; holes may be drilled in it with an ordinary twist drill with practically no damage to the cutting edge of the drill. Its modulus of elasticity is practically equal to ordinary concrete and follows the usual law of behavior. Its compressive strength is as follows:

Pounds per Square Inch	Ordinary Concrete	Superock	Pounds per Square Inch	Ordinary Concrete	Superock
1000	1,000,000	1,200,000	2500	2,500,000	2,300,000
1500	1,500,000	1,500,000	3000	3,000,000	2,700,000
2000	2,000,000	1,900,000	3500	3,500,000	3,100,000

Republic Steel has built a Superock manufacturing plant (Fig. 6) at its Thomas Works in Birmingham, adjoining the blast furnaces, with



FIG. 6.—SUPEROCK PLANT.

facilities for crushing, screening and loading three sizes simultaneously and having a capacity of 1400 tons per day.

Superock is new and necessarily the market must be built up. Its many desirable characteristics of light weight, insulating, acoustic, nailable qualities and its imperviousness to moisture make it an ideal building material. It can be sold at competitive prices per yard with any other aggregates at a neat profit and undoubtedly will help in decreasing cost of pig iron.

#### *Modernized Blast Furnace*

Improvements about the blast-furnace stack have been numerous. In the past few years three major operators within the Birmingham dis-

strict installed ore-screening equipment and are now charging sized ore. Two complete pig-casting machines have been installed and no one is sand-casting iron now in the South.

Furnaces have been enlarged and height increased. There is a trend toward larger diameters of stock lines with resultant decrease in loss of flue dust. Republic's No. 2 furnace had a 14-ft. 0-in. stock-line diameter in 1933. In 1935 it was rebuilt with a 19-ft. 4-in. stock-line gas-passage diameter, having a 17-ft. 0-in. diameter hanging armor. Its volume was increased from 16,387 to 22,355 cu. ft., principally by increased diameter of the upper inwall section and in height as the hearth diameter remained fixed.

Compared with a sister furnace of its 1933 dimensions, the No. 2 produced an average during almost a year as follows: 60 tons more iron per day, 100 lb. less flue dust per ton of iron, 300 lb. less coke consumed per ton, 8 per cent improvement in cost.

A picture of the remodeled No. 2 furnace, showing its symmetrical top loading of the uptakes, downtakes and downcomers, was shown in Crockard's paper (ref. 1).

An automatic electrical clay gun was installed on this furnace and casts are being made under full wind pressure with no slackening whatever. This permits uniform working of the furnace and is of tremendous importance because the complete electrical and steam load for furnaces, coke ovens and coal mines is carried by boilers fired with blast-furnace gas. When the wind is slackened for casting, the gas flow naturally subsides and the boilers suffer; steam pressure reduces, sometimes so that it will not properly operate the blowing engines, and a cycle of trouble disturbs the operation for as much as 2 hr. owing to slackening wind for casting. This trouble has been eliminated by the automatic clay gun, which stops the hole efficiently and quickly under full wind pressure.

Fig. 4 shows that the pressure is continuous, that the furnace is moving itself, and that the wind is not slackened for casting.

### *Improvement in Coke*

A marked improvement has been made in coke, primarily by improvement in the coal-washery practice. A principal and new feature is the jig-bed float control, a device of streamline design, fish shape, that floats on the separation line between the rock bed and the coal. It works the rock-repulsion rotary valve through a series of levers, at a speed commensurate with the proportion of rock, or impurities in the run of mine, or feed, coal. More rock and the bed builds up, raising the float, which speeds up the rock repulsion; less rock and the bed lowers, and the repulsion is slowed down or stopped entirely. Thus a uniform bed of rock is maintained in the jig screens and effects better washing of the coal.

During 1934 one mine washed an inherent-ash coal of 7.86 to 10.76 per cent ash for the yearly average, and considered it a good job, particularly when the run of mine average ash content was 17.43 per cent. By installing jig-bed float controls, this same run of mine coal approximating

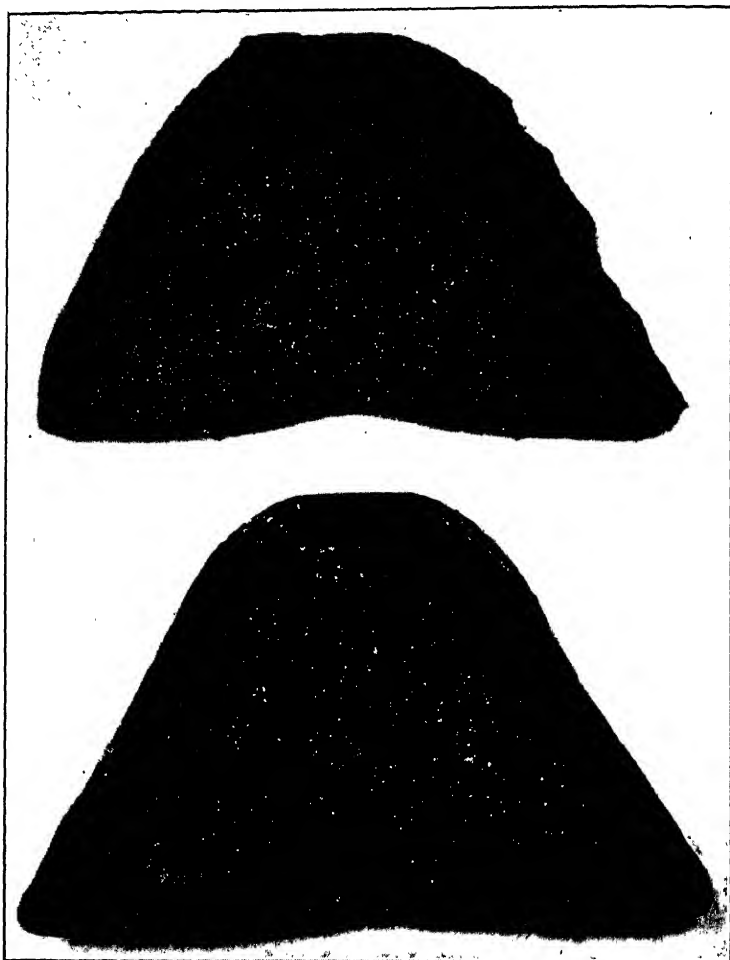


FIG. 7.—PIG-IRON FRACTURES TAKEN PRIOR TO 1930.

Note hard spots and chill or concentrated grain structure at rim of pigs.

17.5 per cent ash was reduced nearly 1 per cent of the 1934 practice to 9.83 per cent ash without appreciably increasing the washer loss. The control of the jig bed was formerly adjusted by hand. The operator felt the bed with a wooden pole, and from experience adjusted the rock-repulsion speed and the hutch withdrawals to control the depth and porosity of the bed, generally on a "hit or miss" basis.

One per cent less ash in the coal is over one per cent more carbon in the coke and obviously a material aid to the blast furnaces—and to

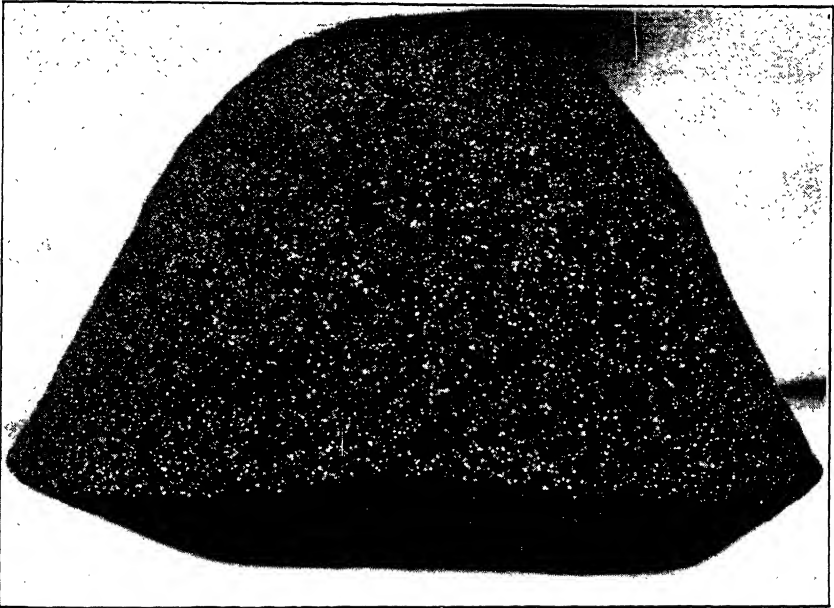


FIG. 8.—UNTOUCHED PHOTOGRAPH OF TYPICAL PIG FRACTURE IN 1936, AFTER IMPROVEMENTS HAD BEEN PERFECTED.

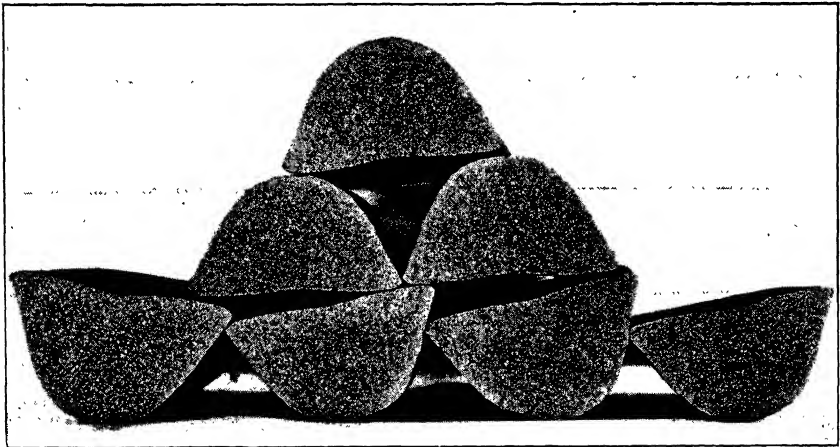


FIG. 9.—SEVERAL PIG FRACTURES SHOWING GRAIN UNIFORMITY AND CLEANLINESS OF IRON.

offsetting increased labor cost. Comparison of test on coke quality shows the improvement:

	Percentages	
	Before	After
Coal pulverization (through $\frac{1}{8}$ in.).....	34.59	76.00
Shatter.....	70.50	82.00
Porosity.....	43.72	40.86
Strength.....	113.65	171.66
Hardness.....	70.75	77.25
Brittleness.....	73.75	25.50
Fuel value.....	131.07	194.40

### *Improved Quality of Pig Iron*

Figs. 7, 8, 9 and 10 are picture stories of the improvements made in the appearance and quality of iron. Fig. 7 is a 1930 machine-cast iron

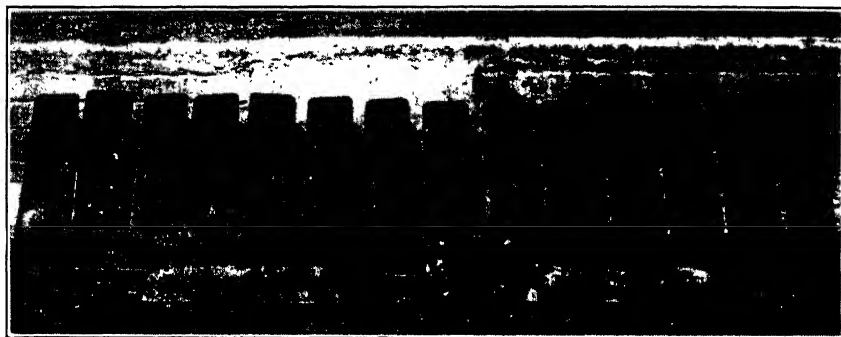


FIG. 10.—TYPICAL 1936 PIGS SHOWING CLEANLINESS OF IRON.  
Note absence of surface impurities, and the smooth surfaces.

fracture and typical of Southern iron of that date. The complete rim has a definite grain concentration, or chill approximating  $\frac{1}{4}$  in.; also a rough surface. Fig. 8 is a fracture of 1936 improved iron, with an absence of chill and a uniform grain. This is a truly representative fracture—not a hand-picked one for show purposes. Figs. 9 and 10 are continuations of this same fact and show the great improvement in the appearance of the iron. To the writer's knowledge, all of the operating iron manufacturers of the Birmingham district are making a clean, smooth iron approaching that shown in Fig. 10.

### CONCLUSIONS

1. Cost of iron manufacture in the South has increased, owing to: (1) increased labor cost, (2) inferior materials, (3) narrowing market, (4) shrinkage of the South's iron business.

2. Wages of Southern blast-furnace employees now almost equal those in other districts.

3. The North-South wage differential is almost a thing of the past at blast-furnace operations.

4. Southern operators have made marked progress in offsetting increased labor cost by mechanization, including: (1) sinter; (2) sized

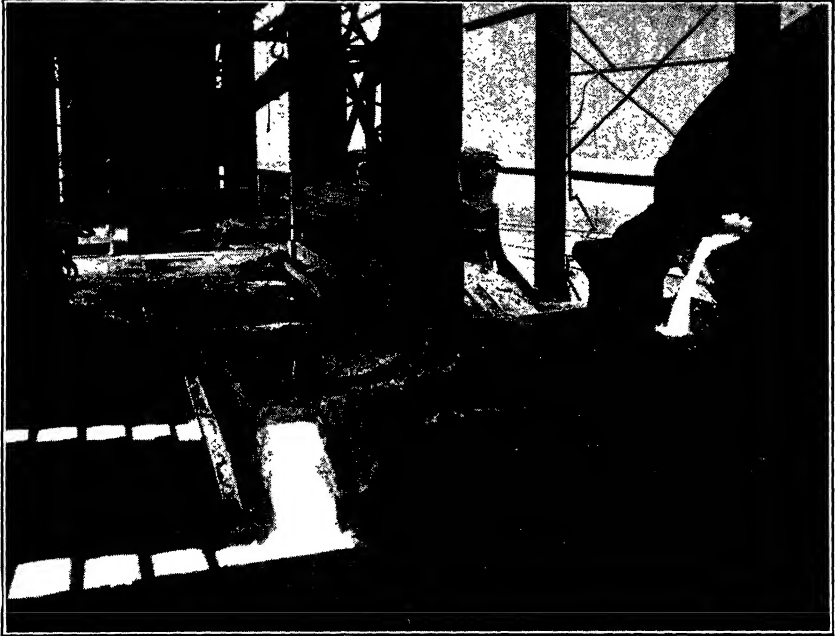


FIG. 11.—SKIMMING TROUGH AT PIG MACHINE.

Showing compartments in trough where kish and impurities floating on molten iron are skimmed off. Periodically these impurities are raked out of the trough and a much cleaner pig iron is produced.

ore, improved raw materials, ore and coke; (3) better furnace operations; (4) Superrock—a new by-product; (5) improved quality of iron.

It is true that there is nothing startlingly new about some of the items mentioned, and they might be classed by some people as elementary; nevertheless in the South they are new and generally represent surviving—holding our own—in spite of increased labor cost.

## DISCUSSION

*(William A. Haven presiding)*

W. A. HAVEN,\* Cleveland, Ohio.—I think those charts show conclusively that the southern district has been meeting its particular problems well. Mr. Hassler has been a little modest in his statement. Several times he said “these things have been done generally in the South.” I believe that is true, but I happen to know that the officials and the personnel of the plant that Mr. Hassler represents have been particularly progressive and a great many of the things described were introduced by them.

\* Vice-president, Arthur G. McKee & Co.



J. T. MACKENZIE,\* Birmingham, Ala.—I think that the introduction of the small pig has been a wonderful help, for the foundry using small cupolas especially. That was initiated in the South, I think, and the change from tapping into a pig bed to tapping into a ladle has been another godsend to the foundry chemist and the metallurgist. It used to be not uncommon to find a difference of 1 per cent silicon between one end of a car and the other end, but now, so long as we are sure that the car came out of one ladle, we would just as soon have one pig as a sample as five. In fact, we have discontinued the old practice of taking one pig for each 10 tons of iron.

We do not operate a foundry that is sensitive to grain size. There seems to be a pretty well defined opinion among the foundrymen that do have sensitive castings that the grain size of the pig iron affects their product, and the step that the southern foundrymen have taken, and which has also been taken up in the North to some extent, is certainly a good thing for the people who have to watch that point.

As one of the figures showed, there was probably a ton from a car of 40 tons that was broken into pieces as small as one's fist. I have seen a pig fly into as many as six or eight pieces when thrown onto a pile, even a pig of 2 per cent silicon cracked all through. We never see a pig iron break in that way now. In fact, the boys taking samples would rather take the whole pig to the drill press than to try to break it up. The paper has very little from that standpoint, dealing mostly with cost, but as a southern foundryman using this pig iron I should like to be on the record as approving the work done in quality as well as cost.

W. A. HAVEN.—Did you say that you believe one of the big advantages of the small pig is to get a more uniform grain structure in the pig?

J. T. MACKENZIE.—Yes.

F. B. THACHER,† Chicago, Ill.—Well, I recognize that the southern merchant furnaces are now doing what some of the northern furnaces have been considering normal practice for some time. It is the competitive situation that makes it necessary to bring about these improvements of product and practice, and the competition is getting keener, not only in the South but in the North as well, not only in production of pig iron but in substitute materials. There is also the desire of the pig-iron producer to cooperate with the foundrymen, who have continually complained about something detrimental in pig iron that was not indicated by chemical analysis.

I think our company can probably take credit for having done the most research work in connection with delicate foundry work, such as making piston rings and things of that sort, where the grain structure does apparently amount to a great deal, and it has resulted in the development of the small pig, in which, we claim, we can control grain structure and carbon segregation. One of the reasons for this research work was the fact that from time to time foundrymen complained about oxidized iron, blowholes and hard spots in castings poured from certain lots of iron, although the chemical analysis was apparently all right. Some castings would have hard spots and blowholes and possibly the remainder of the castings made from the same car of pig iron would be all right.

After a long analysis of the problem we found the cause for this trouble in the working of the cupolas. This was the fault of the pig-iron producer, but it was not a matter of chemistry; it was a matter of physical condition of the pigs. The pigs that formerly we had been making (at least for the past several years) I should say probably averaged at a maximum not over 80 lb., but the molds in which these pigs were made continued to be of the same old size, which in our case would permit pouring pigs up

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\* Metallurgist and Chief Chemist, American Cast Iron Pipe Co.

† Assistant General Manager, Interlake Iron Corporation.

to 125 lb., and in some of the pig molds of the steel companies and others I have seen pigs as large as 150 lb.

The foundryman would burden his cupola for a pig of the average size of, say, around 75 lb., but then an occasional large pig of 125 to 150 lb. would come down through the cupola, and instead of melting at the melting zone it would persist clear down through the cupola to the zone in front of the tuyeres. There free oxygen produced the oxidized or burnt iron that would go out into the pouring ladles and into the castings, causing hard spots, blowholes and bad castings.

Finding that this trouble could be corrected by uniformity of size, our problem was clearly one of producing pigs of uniform size. We now make pigs in molds of about 40 lb. maximum. With this size of mold it is not possible to have the variation in weight formerly experienced, because with the old pigs a variation of from 75 to 125 lb. was a greater difference in weight than the full size of the present pig. While one of the great advantages claimed for the new pig is purely the physical condition of the iron, we also found that by control of size we can control grain structure and carbon segregation. Of course the appearance of the iron can be improved by skimming and keeping out all slag and kish. We all know that with high phosphorus in the iron a much smoother looking pig iron is made than with other types of high-silicon iron.

I am not at liberty to mention names, but I can tell of an experience in a foundry that is making very fine piston rings. The test in that foundry for determining the strength of piston rings is to cut a slot in the ring and then measure pound pressure to close the gap, and the pound pressure to pull open to breaking. There was a variation in strength from 8 to 12 lb. to breaking, using the old type of pig iron. When use of the new type of iron began, the strength jumped up to a uniform breaking strength of 13 to 14 lb. There was not the wide variation previously experienced. This improvement was attributed to iron with more uniform melting characteristics and more uniform grain structure.

My knowledge of metallurgy is rather limited, but I think that the large graphite chunks that are permitted to precipitate out in a slowly cooled pig persist right through the cupola into the casting, and of course there is no strength in the graphite section, which causes the tensile strength in the casting to be materially reduced.

Another advantage of the small pig is that it presents more surface per unit of weight, which facilitates the speed of melting. As a result, there are three advantages; namely, possibility of hotter iron or reduced consumption of coke per unit of iron melted, which in turn may result in increased cupola capacity.

J. T. MacKENZIE.—I should like to have someone write a history of the small pig business. In 1919 the Tennessee Company made for me a carload of pig iron for use in an experimental cupola, 18 in. in diameter, the pigs weighing 40 lb., which we broke into four pieces, each one of which weighed about 10 lb. If anyone else made 40-lb. pigs before 1919, I never heard of it.

MEMBER.—Have you made them continuously since then?

J. T. MacKENZIE.—No, not continuously. Soon after Mr. Crockard went with Woodward, he called a conference of the pipe foundrymen in the district and asked them what size of pigs they wanted and the consensus was one between 40 and 60 lb. As a result of that, I believe Woodward went to a 50-lb. pig. That must have been at least eight or ten years ago.

F. B. THACHER.—Strange as it may seem, the character of the iron seems to persist. I suppose if the iron were held long enough and were superheated it would probably all go back into solution, but that does not seem to be the practice. If there

is a good grain structure in the pig iron the results of use seem to indicate definitely that the character of the pig iron persists straight through into the casting.

W. H. SPENCER,\* Muskegon, Mich.—The effect of the size of pig iron on the physical properties of the metal coming from the cupola may or may not be ascribed to “heredity.” It would seem, however, that there is a much more obvious explanation of the effect of pig size. One of my own experiences with pig iron of varying cross section may serve as an example. The metal was melted in a 42-in. diameter cupola with an eight to one iron and coke ratio. The large pig broken in half weighed approximately 60 lb. per half pig. The metal melted, using one-fourth of this pig in the charge, was unsatisfactory, being sometimes too soft and sometimes too hard. By careful investigation of the melting conditions in the cupola, we found that the bulky rounded sections of the large pigs were not melting in the melting zone proper, but were passing through and even appearing in front of the tuyeres still unmelted. Naturally, this gave a highly oxidized metal. Before the unmelted pig worked down through the melting zone, the metal was sufficiently soft. In this case, no matter how high a quality of pig iron we may have had in the large pigs, we ruined it during the melting operation.

There is no doubt in my mind that we frequently blame on “heredity” conditions that are brought about during the melting operation in the cupola. Whether or not this condition would exist in cupolas of larger diameter, I am not in a position to say definitely, but there does not seem to be any logical reason why the surface-volume ratio of the pig should not be as important in a large cupola as it is in a small one.

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\* Sealed Power Corporation.

## Some Observations Regarding Refractories for Iron Blast Furnaces

By ROY A. LINDGREN\*

(Cleveland Meeting, October, 1936)

SINCE the year 1643, when the first blast furnace in America for treating iron ore was built at Saugus, Mass., out of mica schist quarried in the neighboring district, the procurement of a suitable refractory for furnace lining has been a problem of concern to the operators of furnaces. The stacks built of mica schist continued to smelt iron ore until about 1836, when, according to F. H. Norton, the first firebrick were produced<sup>1</sup>, at Queens Run, Pa. Other writers speak of brick having been molded and burned in Massachusetts about the year 1834.

In 1841, Andrew Russell began to produce medium refractory plastic clay brick near East Liverpool, Ohio, that were used for lining blast furnaces<sup>1</sup>. The well-known Kentucky clay-producing district was not opened up until the year 1871, but since then it has produced a large percentage of the linings for iron blast furnaces.

While some strides have been made by the refractories industry during the 100 years that have passed since the first firebrick were produced, it has been only during the last two decades that any real progress has been made towards bettering the product, even though the method of production had improved. Perhaps the fault lies with the user of the brick rather than with the producer, for not sooner demanding a superior product.

During the past 15 years the tonnage produced per lining has increased from 500,000 gross tons to 1,000,000 gross tons, and now some furnaces are producing 1,600,000 gross tons and better on a single lining. It is true that enlarged capacity of furnaces and improved practice have accounted for some of this increase in tonnage, nevertheless better quality in firebrick must be given credit for its share. However, we are not yet ready to say that we have reached a maximum life of furnace lining. We believe that a better product can be produced and that the refractories industries of America will, through their extensive research depart-

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<sup>1</sup> References are at the end of the paper.

ments, ultimately develop a material that will far eclipse the record so far achieved.

What physical properties should such a brick possess? How closely does the product today meet these specifications? These are some of the questions we shall attempt to answer in this paper.

### FUNCTIONS OF BLAST-FURNACE BRICK

It is obvious, even to the layman, that a brick of one set of specifications will not suffice for lining the entire blast furnace. The hearth and bosh require a brick of a very refractory composition, capable of resisting high temperatures and the slagging effects of molten metal and slag. We believe that such a brick has now been perfected, so that with the present-day method of bosh cooling we seldom hear of a furnace failing through the hearth or bosh, assuming, of course, that proper care has been taken in laying up and drying out as thoroughly as possible prior to blowing in the furnace.

In the shaft of the furnace lies the real problem. Here is required a brick capable of resisting the abrasive action of the stock at temperatures as high as 1800° F.<sup>2</sup> The brick forming the shaft, or inwall as it is called by furnacemen, must also resist disintegration caused by carbon deposition. A blast furnace has often been likened to a huge gas producer, being constantly filled with a gas containing a high percentage of carbon monoxide. The bricks composing its lining are therefore permeated with this carbon monoxide gas at all times. Nesbitt and Bell<sup>3</sup> have demonstrated that carbon monoxide gas in the presence of free iron, or ferric oxide, will break down according to the formula  $2\text{CO} \rightarrow \text{CO}_2 + \text{C}$  if held at a temperature between 788° and 878° F. Therefore, we conclude that the ideal firebrick for blast furnaces must be free of all elements that possess catalytic properties that lead to deposition of carbon within the structure of the brick itself, which create internal strains that ultimately cause the brick to shatter.

### TESTING OF COMMERCIALY PRODUCED BRICK

Bricks produced from various kinds of clay and manufactured under both the stiff-mud and the power-press methods were obtained for the purpose of testing. So that the tests should be representative of actual operating conditions, these bricks were the ordinary run of commercial brick, and were subjected to gas of analyses and temperatures comparable to those encountered in the smelting process.

*Accurate Size and Internal Structure.*—A study of their internal structure was made by grinding the bricks in cross and longitudinal section. Fig. 1 shows these sections. We believe that the ideal brick as outlined in the foregoing should be homogeneous in structure. The bricks produced by the stiff-mud method (Fig. 1a) were laminated. These lamina-

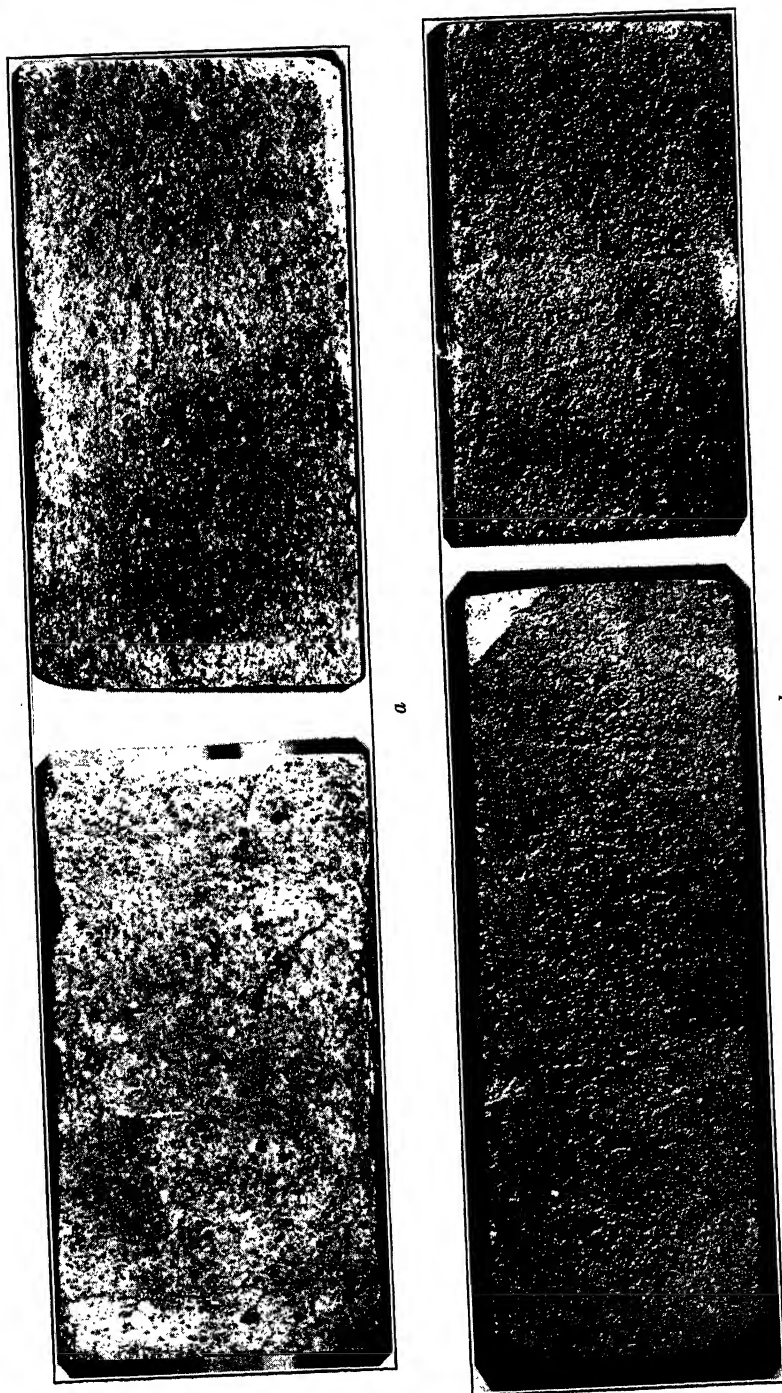


Fig. 1.—SECTIONS OF BRICK SHOWING LAMINATIONS AND POROUS CORE.  
*a*, brick produced by stiff-mud method; *b*, produced by power-press method.]

tions, apparently produced during the extrusion of the clay column through the die, caused planes of weakness and gave ready passage to the furnace gases. In the power-pressed bricks (Fig. 1*b*) there was a segregation of the finer particles of the mixture in the outer surface, causing a dense and hard shell with a soft and porous center. These bricks were also subject to the free access of furnace gas.

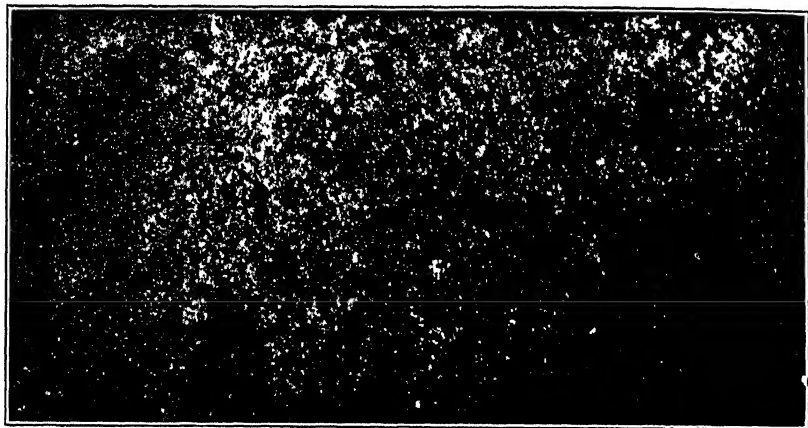
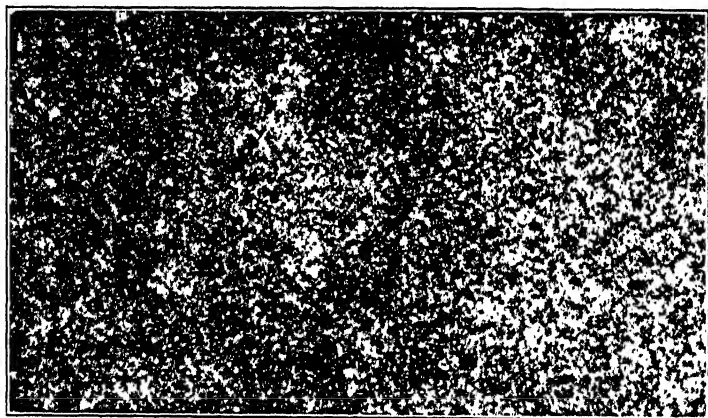
*a**b*

FIG. 2.—SECTIONS OF BRICK SHOWING HOMOGENEITY ATTAINED BY DE-AIRING.  
*a*, brick produced by stiff-mud method; *b*, produced by power-press method.

The refractories manufacturers, in attempting to solve this problem, produced the “de-aired” and the “vacuum-pressed” brick. In producing a brick with all included air removed they have made one of homogeneous internal structure (Fig. 2). In the stiff-mud brick the de-airing process has done much in the elimination of laminations and there is a more homogeneous structure, free from air voids. This is of utmost importance where the tendency is toward carbon deposition

or metallic inclusions such as zinc and lead. The vacuum pressing of brick in the dry-press method has also produced a brick of homogeneous internal structure, giving a more uniform hardness throughout.

The principle of de-airing clay bodies has been known for years but the intensive application of the process has but recently attracted wide attention among brick manufacturers. In its application to stiff-mud machines, the clay body is carried through the evacuation chamber with adequate entrance and exit seals. Therein it undergoes a shredding process before extrusion through the die. This intermediate shredding of the clay column under a 23-in. vacuum is responsible for the results obtained. As applied to the power press, a measured quantity of the clay mix is placed in the mold box, the clay having approximately 6 to 7 per cent of moisture. The cap and lower pad are perforated with approximately 200 minute suction holes connected to the vacuum chamber, which is carried under 23 in. of vacuum. As the cap enters the die, the full vacuum is applied over the entire surface, and as the cap descends the entire pressure of the press (3500 to 5000 lb. per sq. in.) is applied to the top and bottom, with the vacuum effective during the period when the clay mass is in a physical state that most readily permits the flow of its entrapped air.

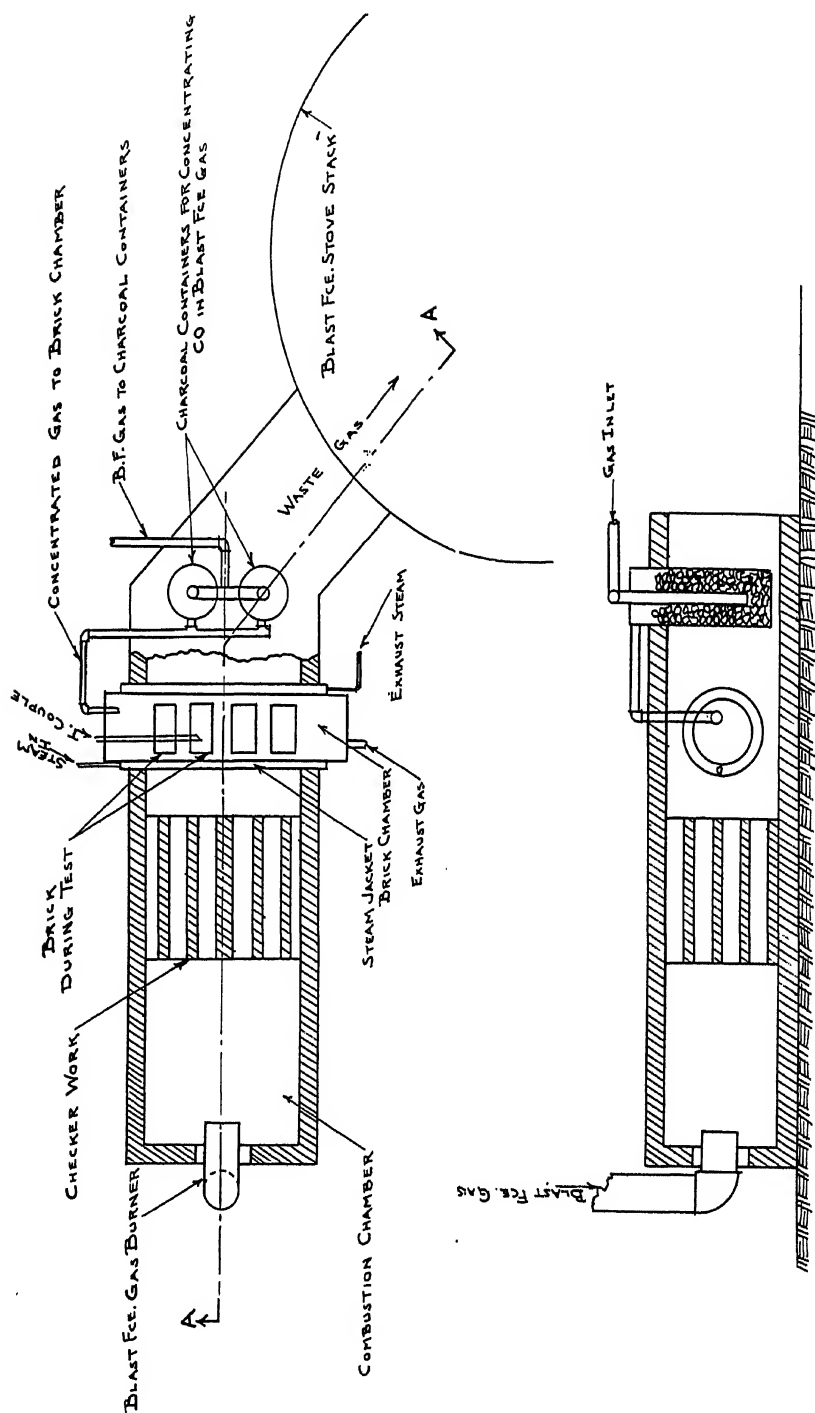
Because of the importance of bricks being free from laminations and porous centers, we are of the opinion that the de-airing of the blast-furnace brick is one of the greatest advances made in the refractories industry during the past decade.

*Importance of Accurate Size and Shape.*—Accuracy to size and shape of blast-furnace bricks is also important. It is just as essential to have these bricks laid up in the lining free from open joints that give easy access to the gas stream as it is to have their internal structure homogeneous. Some designers have considered this sufficiently important to warrant building furnaces wherein special shapes are used in order to break all joints.

Bricks of exact size and true to shape are essential if the lining is to be laid up gastight. Methods of laying up linings are more or less similar in various plants, but no matter what kind of bond is employed, bricks of exact size and shape are essential in producing a gastight lining. It is generally conceded that the bricks produced today are far superior to those made by the old hand method, but we still find that manufacturers, in spite of modern equipment, are grinding the finished bricks to size in order to hold to the close tolerances now required. It is our opinion that the answer to accurate size of bricks will be found not in more accurate methods of shaping the "green" bricks but in the firing of the bricks in the kiln.

*Tests to Determine Tendency towards Disintegration.*—Considerable work on the disintegration of brick by carbon deposition has been done





SECTION A-A  
 FIG. 3.—FURNACE FOR TESTING BRICK FOR DISINTEGRATION.

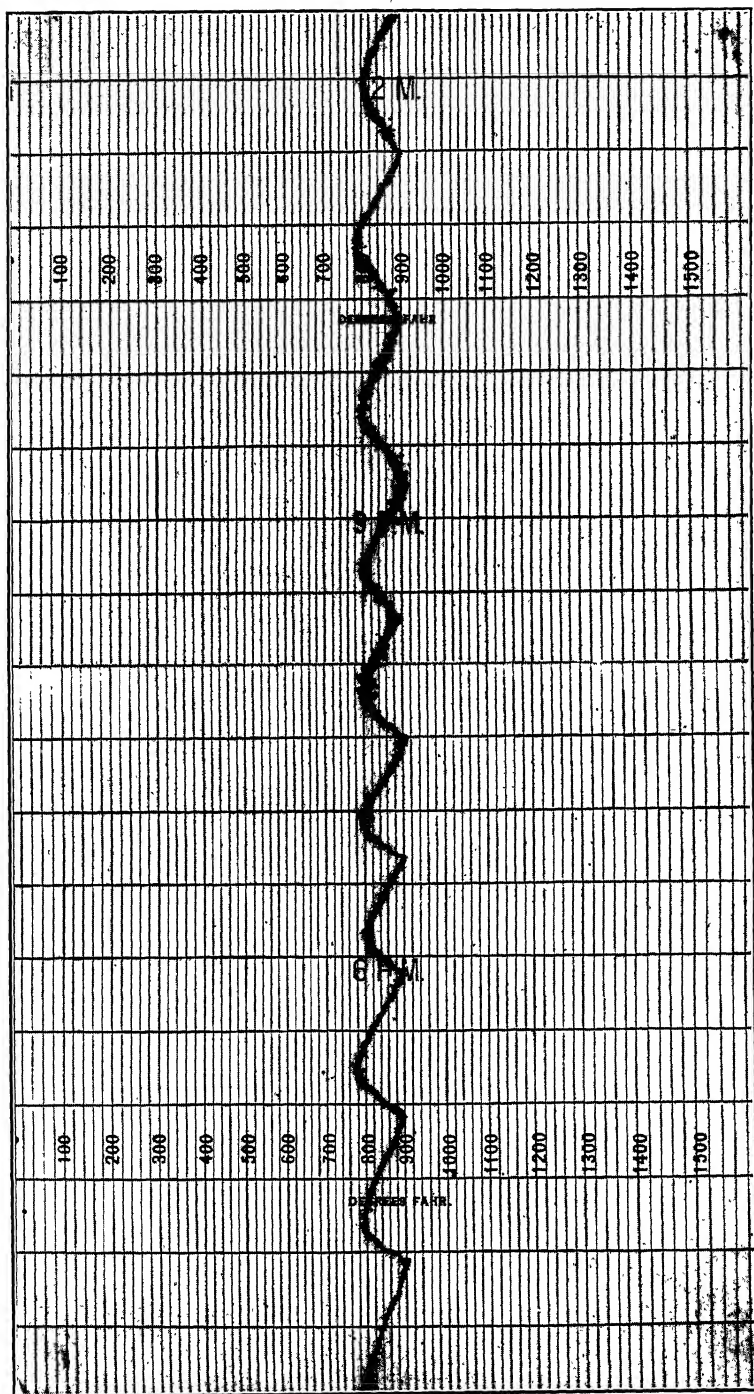


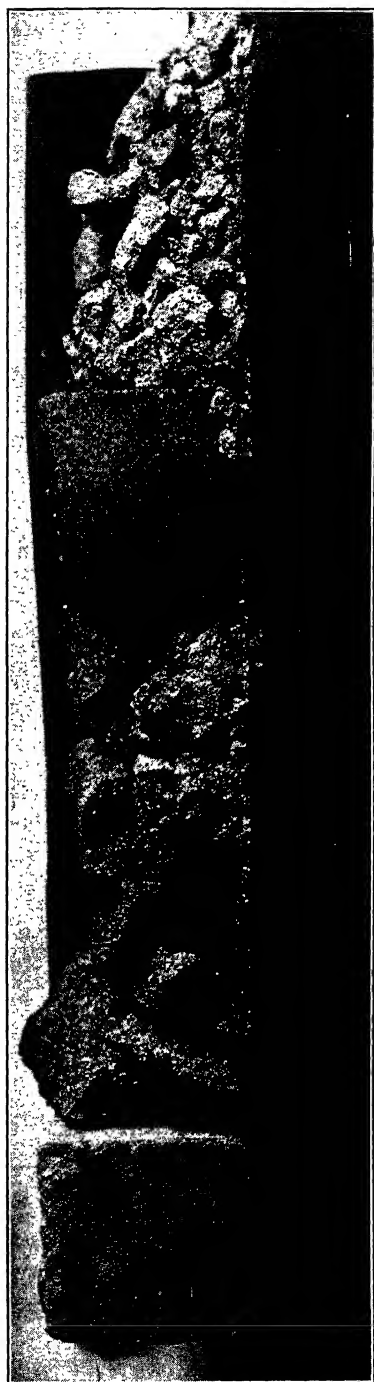
FIG. 4.—TEMPERATURE OF BRICK DURING DISINTEGRATION TEST.

in the laboratories. We endeavored to subject commercial brick to conditions as near as possible to those existing under actual operation. A small disintegration furnace (Fig. 3) was built near the blast-furnace stoves so that fuel in the form of blast-furnace gas was readily available. The furnace consists of a combustion chamber in which ordinary blast-furnace gas was used as a fuel for heating the testing chamber. This testing chamber consisted of a 10-in. diameter pipe inside of a 12-in. diameter pipe welded together to form a jacket around the 10-in. pipe. Into this annular jacket space was piped steam, which was used as a cooling medium in order to swing the temperatures through the critical range of 788° to 878° F. Into one end of the test chamber was piped blast-furnace gas under pressure, enriched in carbon monoxide by passing it through hot charcoal. The analysis of the enriched gas varied as follows: CO<sub>2</sub>, 9.6 to 6.0 per cent; CO, 32.0 to 37.6; H<sub>2</sub>, 4.2 to 6.4; CH<sub>4</sub>, 0.4 to 0.2. This approximates the analysis of the gas up through the stack of the blast furnace<sup>2</sup>.

TABLE 1.—*Representative Tests*

Duration of Test, Days	Designation of Sample	Iron Analysis, Per Cent		Results
		Fe as Oxide <sup>a</sup>	Total Fe	
9	A	0.50	1.81	No sign of disintegration.
9	B	0.80	2.21	Disintegrated into rather large pieces.
9	C	0.60	2.01	Disintegrated into rather large pieces.
9	D	0.70	2.01	No disintegration.
9	E	0.60	1.81	Completely shattered; very small pieces.
9	A	0.81	2.01	One piece ½-in. dia. on surface broken off by small piece of carbon deposited ¼ in. under.
9	B	0.81	2.21	Badly cracked; one very large crack, which split brick in two.
9	C	0.81	2.21	Partly shattered, large pieces of carbon (½ to ¾-in. dia.) deposited and expanded.
9	D	0.91	2.21	No sign of disintegration.
9	E	0.70	2.01	Completely shattered into very small pieces. Small carbon deposits throughout.
7	A	0.41	1.53	Split in two pieces by large carbon deposit.
7	B	0.51	2.22	No sign of disintegration.
7	C	0.51	1.92	Completely broken into large pieces.
7	D	0.61	2.02	No sign of disintegration.
7	High Al <sub>2</sub> O <sub>3</sub>	0.51	1.52	No sign of disintegration.

<sup>a</sup> Iron soluble in hydrochloric acid.



A

B

C

D

E

FIG. 5.—BRICKS AFTER DISINTEGRATION TEST.  
See Table 1 for descriptive data.



A

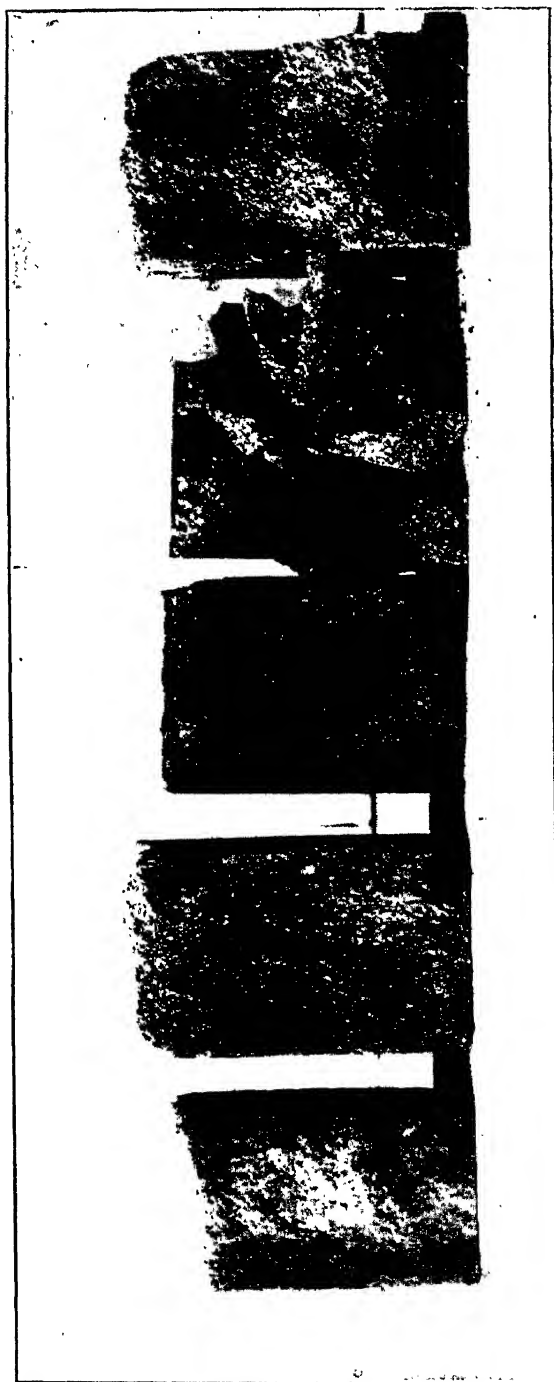
B

C

D

E

FIG. 6.—BRICKS AFTER DISINTEGRATION TEST, SHOWING EFFECT OF LARGE CARBON DEPOSITS.  
See Table 1 for descriptive data.



High  $\text{Al}_2\text{O}_3$  Brick

B

D

C

A

FIG. 7.—BRICKS AFTER DISINTEGRATION TEST, SHOWING COMPARATIVE EFFECT OF LARGE AND SMALL CARBON DEPOSITS.  
See Table I for descriptive data.

*Method of Testing for Disintegration.*—In each test five samples were run simultaneously. (Bricks of certain makes are designated by letters in Table 1.) During the test the temperature within the test chamber was measured on a recording pyrometer and controlled by the operator. Fig. 4 is a reproduction of a portion of that pyrometric record. Temperature control was effected by the use of steam in the jacket around the brick chamber. Thus, when the temperature reached 900° F. the steam was turned on and the chamber cooled to 800° F., after which the steam was shut off and the temperature again permitted to reach 900° F. This cycle required about an hour, so that in the course of a day the bricks were passed through the critical range about forty-eight times. Some bricks shattered within two days; others required up to seven days. Bricks that did not fail within seven days could not be disintegrated, even though tested for a period of three to four weeks.

A great many tests were made over the period of a year but for the sake of brevity only a few representative ones are described here. In Figs. 5, 6, and 7 are shown the results of a few of the tests.

*Quantity of Iron Does Not Indicate Tendency towards Disintegration.*—From a study of the foregoing we are led to the conclusion that neither the percentage of total iron nor the percentage of iron oxide indicates whether or not a brick will disintegrate. In 1923, Nesbitt and Bell concluded that the percentage of ferric oxide was a direct indication of the rapidity and amount of carbon deposition. In our tests upon commercially produced brick we were not able to verify this conclusion. We failed to find that the percentage of either iron oxide or total iron gave any indication as to the susceptibility of a brick toward carbon deposition and subsequent effect of disintegration. Notice in Table 1 that bricks marked D did not break down during any test. Comparison of their iron analyses with those of the other bricks tested shows them to be higher in both iron oxide and total iron than some bricks that completely shattered under the same test. Notice also bricks marked E, which were completely broken down in each test. Bricks marked D and E were produced by the same manufacturer from different clay bodies of similar analyses. If the process of manufacture, as regards the drying and burning of the brick, was similar in both cases, we believe that some inherent quality in the clay has caused one to produce a nondisintegrating brick and the other, a brick that is easily disintegrated.

The recent work of C. C. Furnas<sup>4</sup> on the problem of why some bricks show a greater tendency towards disintegration than others gives an explanation of this. In the published results of his experiments he states that a determination of the amount of iron oxide present does not indicate a tendency toward disintegration, but that the degree of oxidation of the iron present does tell definitely whether or not the brick will disintegrate. He concludes that if the iron oxide in the brick is in the

form of  $\text{Fe}_3\text{O}_4$  carbon deposition will not occur, whereas if it is present as  $\text{Fe}_2\text{O}_3$  the decomposition of carbon monoxide and deposition of carbon is positively catalyzed. If this theory, which is the result of laboratory experimentation, can be successfully applied to commercial production we may soon obtain bricks impervious to the deposition of carbon, with its resultant effect of disintegration.

*Disintegration Does Not Necessarily Mean Lining Failure.*—The ideal brick for a blast-furnace lining should not disintegrate, and such a brick will give a longer service than one that shows tendencies towards dis-

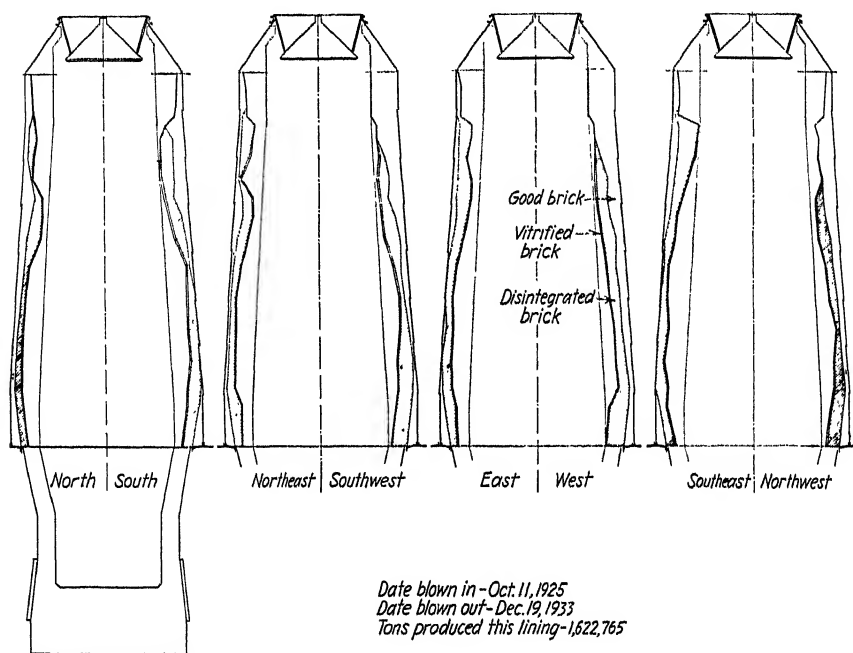


FIG. 8.—BURNED LINES AND SECTIONS THROUGH LINING, TAKEN ON FOUR AXES.

integration; provided, of course, that it combines with this quality the other qualifications of a blast-furnace brick as to hardness, density and workmanship.

However, furnaces have produced large tonnages on linings that have been badly disintegrated but in such cases the furnace has been able in some way to overcome failure due to disintegration. A furnace that had produced 1,622,000 gross tons of iron during its campaign was found, after blowing out, to be disintegrated throughout the entire lining that remained in the furnace. Fig. 8 shows the burned lines and sections through the lining taken on four axes. The question arises as to how this furnace was able to produce so large a tonnage with the lining badly disintegrated.

The process of disintegration, we believe, begins with the blowing in of a furnace. This has been proved by drill-testing the lining of a furnace in blast. The lining of a furnace blown out after one year's run was shown by drill testing to be disintegrated, although the working lines of the stack appeared to be in perfect condition. At 10 ft. above the mantel, disintegration had started at a distance of 12 to 14 in. from the

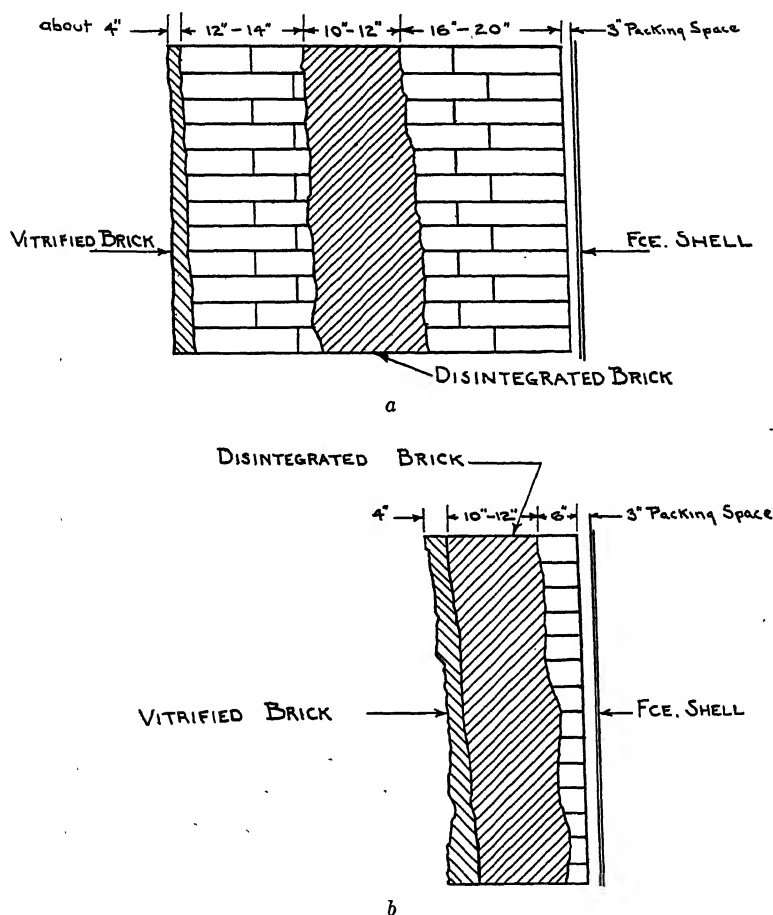


FIG. 9.—PROGRESS OF DISINTEGRATION: (a) AFTER FIRST YEAR; (b) WHEN BLOWN OUT.

face of the lining and continued through the lining for 10 or 12 in., leaving 16 to 20 in. of good solid brick to the furnace shell. This furnace had the same thickness of lining as that shown in Fig. 8, where it is shown that, upon blowing out, the total thickness remaining was only about 18 in. at the same height. Assuming that after a year's run the same condition existed in both furnaces, we find that the disintegrated area has moved back toward the shell as the face of the lining wore away, and that



a hard wearing surface, monolithic in appearance, has formed on the lining face. The lining face, after finishing the campaign, had worn back to the point where disintegrated brick had been found at the end of the first year's service. This is illustrated by the sketch in Fig. 9. A portion of the highly vitrified wearing surface was removed and analyzed, as was the shattered brick immediately adjacent to it. These analyses are compared to the analysis of the original brick, in Table 2. The analysis of the vitrified brick is higher in iron, carbon and alkalis. This change in composition probably has altered the physical characteristics of the brick to the extent that vitrification takes place at much lower temperatures than in brick of the original composition.

TABLE 2.—*Analyses of Brick Taken from Furnace Lining That Has Produced 1,622,000 Gross Tons*

	Vitrified Face of Lining When Blown Out, Per Cent	Disintegrated Brick Back of Face, Per Cent	Original Brick, Per Cent
Fe <sub>2</sub> O <sub>3</sub> .....	1.71	1.86	2.29
FeO.....	1.37	0.68	0.26
Fe (metallic).....	0.17	0.17	
P <sub>2</sub> O <sub>5</sub> .....	0.036		
MnO.....	0.11		
SiO <sub>2</sub> .....	44.78	52.74	54.52
Al <sub>2</sub> O <sub>3</sub> .....	31.71	42.30	42.56
CaO.....	1.68	0.49	0.44
MgO.....	0.68	0.47	0.35
Carbon.....	7.21	1.03	
SO <sub>3</sub> .....	0.057		
K <sub>2</sub> O.....	3.56	0.17	0.27
Na <sub>2</sub> O.....	5.32	0.12	0.10

It is thought that what takes place is a reburning, or vitrification, of the disintegrated brick to form this wearing surface, and that as long as proper distribution of stock and wind is maintained it will suffice to enable the furnace to give a normal tonnage on a lining. As a check on this theory, a portion of the disintegrated brick was carefully removed without crumbling, in order to maintain its semblance to the original brick shape, and then placed in a muffle furnace and reburned under reducing atmosphere at a temperature of 3000° F. The disintegrated brick was vitrified and in a sense reburned. It greatly resembled the original brick, and, although brittle, had considerable resistance to abrasion.

We propose this as the answer to the question of furnaces producing normal tonnages on badly disintegrated linings and we believe that should a furnace lining disintegrate it does not necessarily fail from that cause alone. We are convinced that if the stock distribution is closely checked along with the maintenance of proper tuyere area and wind velocities

the furnace will form the necessary wearing surface as the lining wears back, thus enabling the realization of a normal tonnage even though the bricks have been disintegrated.

#### CHECKER BRICK FOR BLAST-FURNACE STOVES

Several failures of checker brick in blast-furnace stoves have occurred in the past five years. These failures have been of two types: (1) the erosion of the checkers due to a melting down of the outer skin of the brick, which on cooling causes a chipping off of the good brick beneath, and (2) a large secondary shrinkage, which causes a structural failure of the checkerwork.

High blast temperatures ushered in stoves of large heating surfaces, along with the fine cleaning of blast-furnace gas. While not sufficient research has been carried out to substantiate any theory, certain brick manufacturers lean to the hypothesis that the fine cleaning of gas leaves certain elements in the gas, without the neutralizing effect of elements now removed, that cause an alloying with the material composing the brick and thus change its physical characteristics as to softening point, shrinkage, etc. Research work is now underway to determine corrective measures to be applied in solving this problem. Whether this will result in a brick of new composition or a change in gas-cleaning methods remains to be seen.

#### CONCLUSION

We have attempted to outline some of the advances that have been made and the problems still to be solved in perfecting a superior refractory for the lining of the iron blast furnace. The necessity for accuracy of size and shape, the requirement of a homogeneous internal structure, and the problem of disintegration of brick in a lining have been discussed. We have noted the results already obtained in reference to some of these problems, and the need for further work in others.

The refractories industry has made great strides in an attempt to furnish a brick better suited for lining blast furnaces. It has established research departments that are working constantly on the problem of better brick. However, the surface has been merely scratched to date, and we, the consumers, must stand prepared to aid by collecting and correlating data that will be beneficial in this research work.

Such data as a record of the dome temperatures of stoves, periodic analyses of the dust content of the furnace gas, analyses of the dust deposited on checker brick, analyses of brick from furnace linings, and deposits of foreign elements in the brick, are all valuable to the research engineer. The commercial magnitude of the blast-furnace installation forestalls any attempt to reproduce operating conditions in the laboratory, so the research engineer must come to the furnace operator to

prove or disprove his theories. Only by such cooperation can we hope to arrive at a solution of the problem of suitable refractories for the iron blast furnace.

#### ACKNOWLEDGMENT

Acknowledgment of assistance is made by the author to Mr. W. E. Brewster, Superintendent of Blast Furnaces, Wisconsin Steel Works, and Mr. P. R. Nichols, Assistant General Foreman of the Blast Furnace Department.

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#### DISCUSSION

(*William A. Haven presiding*)

J. C. HOPKINS, Cleveland, Ohio.—Mr. Lindgren, as a blast-furnace operator, was rather modest in his remarks as to the minor part the blast-furnace operator and engineer have played in the improvement in linings from a half million tons up to one and one-half million tons which are common today, because it has been only through the cooperation that the brick industry has had from the blast-furnace fraternity that those results have been possible. All of us that have large research departments and are spending considerable money on research work do want to cooperate with the blast-furnace people in an endeavor to improve the tonnages.

J. S. UNGER, Pittsburgh, Pa.—For a great many years I have been interested in studying refractories, having done a great deal of work along the line of firebrick, magnesite and chrome brick, looking toward the improvement in manufacture. Mr. Lindgren's paper has tried to base the quality of the brick on the tonnages made. This is a mistake, gentlemen. It depends upon what you are doing with the blast furnace. You may get 1,600,000 tons on a lining of a blast furnace making pig iron, but if you are making ferromanganese you had better make up your minds that you are not going to get anything like that tonnage. The difference in the making of a ferromanganese and pig iron is in the intensity of the reduction. We know that our temperatures in a ferro furnace are very much higher than in the pig-iron furnace. We know that the gases coming from a pig-iron furnace carry, in round numbers, 24 per cent CO<sub>2</sub> and in a ferro furnace about 36 per cent CO<sub>2</sub>.

A furnace that has been blown out after it has been running on ferro will show a very much thicker zone of disintegration of the lining from the top to the bottom. The bricks will be disintegrated to a much finer powder, and so much disintegrated that about 10 ft. from the top of a ferro furnace the disintegrated brick will show up almost at the surface, and instead of extending down to the mantel, which is about as far as the average pig-iron furnace disintegrates, I have seen it extend to very close above the tuyeres.

Disintegration does not necessarily occur from an atmosphere of carbon monoxide. In addition there must be a catalyst and the proper temperatures. In only one or two cases have I ever seen disintegrated brick in a hot-blast stove. The blast furnace seems to be the principal offender. There is some disintegration in the cupola and gas producer; not so much as in a blast furnace.

The brickmaker naturally makes his bricks by the most economical process he can use and still preserve the commercial quality. I do not believe the user of the brick has given the brickmaker all the information he should have. I do not think the brickmaker really knows what happens in the blast furnace. The brickmakers make the bricks and send them to the customer and they do not really know what he is going to do with the bricks. They do not understand that he may put some of them in a blast-furnace. He may specify firebrick, and the manufacturer will send him a mill grade of bricks, not knowing that they are going into a blast furnace. If he specifies blast-furnace lining he will order so many hearth and bosh bricks, so many inwall, and so many top bricks.

If I do say it myself, thanks to the discussions and conferences I have had for the last 15 years with the principal brickmakers, I believe that I was partly responsible for forcing some improvement in the making of blast-furnace brick.

If you are making tests and want to determine whether the brick is fit for the purpose intended, you must make your tests quickly; therefore, we had to use concentrated carbon monoxide, and in our work we used carbon monoxide that was averaging 80 to 90 per cent of CO, which is very much higher than you find it even in the ferro furnace. That gave us real results quickly. We had to have results quickly. We said that a brick that would stand 40 hr. in a disintegration furnace without serious disintegration was fit for the purpose intended.

Going back to the test in which we added very fine powdered iron ore and others with coarser lumps, we found that the brick with the very fine particles uniformly distributed throughout would show fine cracks. They could be seen with a hand glass. They were uniformly distributed through the brick but the brick was not disintegrated, but where we had the larger particles like raisins in a cake that gave a larger nucleus the carbon was immediately deposited and would break the brick apart. The iron in the brick must be in a certain form to cause disintegration. A chrome brick, which may carry 20 per cent iron, does not disintegrate. A magnesite brick with, say, as much as 8 per cent iron, does not disintegrate.

In a silica brick we deliberately determined to make a certain quality that would disintegrate. We put as much as 3 per cent iron oxide into the brick. You would say that ought to disintegrate at once. It does not do it because the iron in the burning is combined with the silica, forming ferrous silicate, which is inert. The iron to cause disintegration must be in one or two forms, either metallic or as a ferric oxide,  $\text{Fe}_2\text{O}_3$ . The brickmaker has striven to prevent the disintegration of bricks by pursuing a practice in which he burns his bricks, up to cone about 8 or 9, and then he tries to finish the burn with a reducing atmosphere, giving an atmosphere with carbon monoxide, and this atmosphere reduces the ferric oxide that may be there to magnetic oxide, which does not disintegrate nearly as rapidly as the ferric oxide. The magnetic oxide alone will not produce disintegration; neither will the ferric oxide produce disintegration. It must be accompanied by a small quantity of metallic iron to get the proper catalyst. The thing that makes the brick break up or disintegrate is a mixture of ferric oxide and metallic iron.

The brickmaker can improve his bricks a great deal by preparing a clay that is absolutely free from iron. The only way that could be produced commercially would be to give the clay an acid treatment and dissolve out the iron. Magnetic concentration is hopeless. I am speaking now of a brick firm that went so far as to concentrate its clay magnetically, hoping to take out the iron to begin with. It

discovered it was necessary to heat the clay up to a temperature of about 500° F. to convert the iron into the magnetic state. This drove off the combined water and destroyed the plasticity of the clay. We had a difficult time making brick out of it later. The only thing the brick maker could do was to finish the burn under a reducing atmosphere to convert what iron was there into a magnetic state. A few hours before he shuts the kiln down, he raises the temperature so as to compel what iron is there to combine with the free silica in the brick and form ferrous silicate, as that is inert, just as it is inert in a silica brick, a chrome brick or a magnesite brick.

The author referred to a change in brick composition during use. (Nesbitt and Bell's paper<sup>3</sup> shows the analysis of a number of bricks. It gives the iron content before they were put into a lining, and after approximately a million-ton campaign they were again analyzed.) We found the iron, as I remember the figures, had increased to about four times the original amount, the alkalies had increased from a few tenths of a per cent up to the worst case, 6 per cent, and a new element had entered into the brick that was not there originally, and that was carbon.

If bricks change in composition as much as I have just indicated, it seems that even if the manufacturer should begin with very pure material the user would still have trouble from the absorption of some of these new compounds, alkalies, which very materially reduce the refractoriness of materials and also the absorption of iron and carbon. I do not think we have given the brickmaker a square deal. We have kept on pounding him about the quality of his bricks, and he did not know what was the matter or how to correct it.

I said early in the discussion that the brickmakers did not approve my suggestions from the very beginning, because anything that I would suggest meant an increase in the cost of the bricks. I think they are learning. I am thinking now of one that makes all his blast-furnace bricks dry-pressed. They are true and straight. He follows every burning in the kilns carefully by making disintegration tests. I talked with a young man in this particular brickmaker's laboratory, who said, "We do not need to make disintegration tests any more. We can tell whether or not they are going to disintegrate quickly by the burn. If they are fairly soft they disintegrate quickly because the iron has not been converted to ferrous silicate. If it is a hard burn it has been converted and it will not disintegrate quickly."

We are getting better brick than we ever got before, but do not expect too much from the brick. My own opinion is that 1,600,000 tons means nothing. The average blast furnace after it has made about 750,000 tons ought to be blown out and relined to provide for the erosion and preserve the original lines.

O. R. RICE, \* Chicago, Ill.—My experience with disintegration was obtained at the time that I was connected with operation, and I want to point out an interesting factor that shows how, in investigating a topic, circumstantial evidence that sometimes appears very clear and plain may lead one down the wrong track.

A furnace was relined after the war; the lining was bought during the war at a time when things were pretty hurly-burly and perhaps quality was not the first criterion or the first possibility, and after making approximately 300,000 tons the furnace shell developed serious cracks in the horizontal joints. The joints separated and continued to separate until an opening of as much as 8 in. occurred, raising the top of the furnace, rupturing the connections to the skip incline, and necessitating shutting down the furnace.

We made a very exhaustive investigation of the state of the lining. We had used in the burden a zinc residuum from a by-product from the zinc-manufacturing concern, which also had been used in making spiegel, and we knew that on the spiegel operation, lining practice had been short-lived. We used only about 10 per cent of

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\* Freyn Engineering Co.

this zinc residuum, but inasmuch as it contained several per cent of zinc we felt that circumstances indicated that zinc was at the bottom of the difficulties experienced. We early found that the reason the shell had ruptured was that the brick lining had expanded vertically. As I say, we made exhaustive investigations of the state of the brick lining, taking samples at elevations of every two feet as we tore the lining out and at every several inches horizontally across the face of the brick wall. The brick lining itself was in place, in the furnace, perfectly sound brick for the first foot or two back from the wall face and perfectly sound the last foot or two toward the shell. In the center was a zone of complete disintegration, so that the material could be shoveled out between the two firm walls. I might say parenthetically that the joints between the bricks were there and in place and hard and sound, so that the disintegrated "gravel" or "powder" could be picked out between the joints as sand out of little boxes. There was the zinc. It did not take any chemical analysis to show that there was the zinc. It could be picked up with the fingers. There were pounds of it in metallic form. The string of circumstances was certainly clear and obvious, and there was only one flaw in the circumstances. The pieces of zinc we found there were round, like so much shot. It hardly seems likely that the zinc if it had been the cause of disintegration and the lifting of the lining would be there in the round state as shot. It would be there as an infusion. Ultimately we did chase down the real cause of the trouble, which was the precipitation of carbon not only in the brick but also against the surfaces of the iron wearing plates in the top of the furnace. We accounted for 50 per cent of the raise of the shell by layers of carbon deposition between these metallic wearing plates, bearing out what Dr. Unger says, that there must be a certain amount of metallic iron present to act as a catalyzer, and the wearing plates were beautiful providers of that catalyzer.

A. G. McKee, \* Cleveland, Ohio.—Developments have been going along, and I think the brickmaker has done a very good job and is in the way of making a still better job in developing bricks that are better suited for all the various purposes. I can well remember when I remarked to a brick manufacturer that the best paid man in the plant should be the fellow who picks out the samples. It was really pertinent. That is amusing but not pertinent at the present time.

I rebuilt a furnace for the New Jersey Zinc Co. a few years ago, and the lining swelled up like a poisoned pup. The bricks did not disintegrate appreciably, but when the bricks were taken out they ranged from a tinge of purple to purple all the way through. I did not analyze them but I was told that it was caused by a very large amount of zinc. The lining swelled so that it pushed the shell apart and broke the furnace columns. That makes me think that possibly the expansion mentioned was in the firm brick, not the disintegrated brick, and that added to the carbon deposition on the top plates made up the total of the expansion of the lining.

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\* President, Arthur G. McKee & Co.

## Raw Coal in Blast Furnaces

BY W. T. ALLAN\*

(Birmingham Meeting, April, 1937)

Raw bituminous coal has been in general use as a blast-furnace fuel in Scotland for the last century, and although its use has now been largely abandoned and it has been replaced by coke in the majority of the few furnaces which are at present in blast in this country, coal-smelted pig iron is not yet a thing of the past; it is still being produced and marketed in competition with the more cheaply smelted product of the coke-fired furnace.

Various factors have influenced this change in practice; the once plentiful deposits of coal of a suitable nature for the blast furnace are now not so easily obtainable; native blackband and clayband ironstones which are easily smelted in the coal-fired blast furnace, although still far from being exhausted, are not available except at a cost that is somewhat higher than that of imported ores, making them unattractive to the ironmaster that is compelled by circumstances to smelt his iron at the lowest possible cost. Within the last 15 years overproduction of synthetic nitrogen has led to progressive reductions in the price of sulphate of ammonia, the recovery of which together with the other by-products before that time materially assisted in reducing the working costs of the coal-fired furnace. Now the sale of the by-products recovered yields a diminished profit.

When the cost of the product is the only consideration the small, slow-smelting, coal-fired blast furnace cannot compare with its large, modern, coke-fired competitor. Other considerations do not by any means all support the same side of the argument. In the smelting of pig iron to be used in the manufacture of steel where the quality of the final product depends so largely upon the control of the conversion process and so much less upon the physical quality of the pig iron used, the physical properties of the pig iron do not exert any appreciable influence upon the quality of the steel produced, therefore the methods employed in the smelting of the pig iron matter but little so long as the requisite chemical composition is reached. On the other hand, in ironfounding where the simple melting of the pig iron, which is the only treatment it receives before being cast into its final form, does little or nothing to modify its original charac-

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teristics, the physical properties of the pig iron are largely retained in the casting, and because of this they are of considerable moment to the iron-founder. The physical properties referred to are not the figures obtained from physical tests made upon the pig iron but are those elusive "inherent" virtues which are impossible to express quantitatively, are not always recognized by orthodox opinion, but whose existence is undoubted by the experienced practical foundryman. Those inherent properties arise partly from the method employed in the smelting of the pig iron and partly from the materials from which the pig iron is smelted and cannot be evaluated by any known method of chemical analysis or of physical testing.

In the same manner, if not in the same degree, as cold-blast pig iron differs in its inherent properties from hot-blast pig iron so does coal-smelted pig iron differ from coke-smelted pig iron. The different conditions obtaining in the hearth of a cold-blast furnace compared to a hot-blast furnace are sufficient to lead one to expect differences in the two products; differences between the reduction processes in the coal-fired furnace and the coke-fired furnace are not, perhaps, so obvious.

The principal factor leading to altered conditions is undoubtedly the presence in the furnace of tar distilled from the coal. The tarry vapors impregnate the ore during its descent of the furnace shaft, condense upon the surface and within the pores of the ore and later, as the ore reaches hotter regions of the furnace, the deposited tar is subjected to distillation, leaving a residue of coke upon and within the ore. The presence of this protective coating of tar must have a hampering effect on the first stages of the reduction process by carbon monoxide, which occur very early in the coke-fired furnace, and may quite conceivably inhibit it until such time as the coke which is formed on the distillation of the tar has been removed either through solution by the ore or by the  $\text{CO}_2 + \text{C} = 2\text{CO}$  reaction. These reactions will again be delayed by the absorption from the furnace gases of the heat necessary for the coking process, the absorption of this heat altering the temperature gradient of the coal-fired furnace as compared to the coke-fired furnace. The deposit of tar coke upon the ore will also hinder the catalytic  $2\text{CO} = \text{CO}_2 + \text{C}$  reaction.

The presence of hydrocarbons and a greater proportion of hydrogen in the gases of the coal-fired furnace and the consequent reduction of some of the iron through their agency, together with the indirect effect of hydrogen on other furnace reactions, may affect the properties of the resultant pig iron. Although the coal is coked by the time it reaches the tuyeres of the furnace, the coking process takes place while the coal is sustaining the weight of the burden above it, with the result that the coke formed differs from the coke-oven product and does not lend itself to unduly rapid combustion, with its consequent generation of intense heat at the tuyeres. In a furnace using part coal and part coke, it is an easy matter to tell



from observation at the tuyeres which fuel is being burned at the time of observation, the more lively appearance of the latter being most marked.

It may therefore be conceded that differences enough exist to lead one to expect a different product from the coal-fired blast furnace, apart altogether from the slower rate of driving which, with some reason, is often stated to be the principal cause of the superior qualities of coal-smelted pig iron.

The combination of the processes of coking and ore reduction in one piece of plant is one great advantage of the coal-fired furnace, saving capital costs and, indirectly, working costs. The small furnaces to which the coal-fired furnace operators are irrevocably tied, while they prohibit large outputs with their accompanying small overhead costs, are an advantage in times of dull trade when stocking problems become insurmountable for the furnaces of very large outputs. Another advantage is the comparative ease with which they may be switched from one type of iron to another; to the ironmaster engaged in smelting steelmaking pig irons that is of little or no account, but to the producer of foundry pig irons with their numerous and widely varying specifications it is a matter of great importance.

While the future of the coal-fired furnace is obscure and would appear to wear a forbidding aspect so far as the smelting of steelmaking pig irons is concerned, there is every reason to suggest that its continued operation will be justified by the continued demand for the high-grade foundry pig iron which in the past has won a world-wide reputation for Scotch pig iron. Should it prove otherwise, the stockyard of the foundryman who makes engineering castings will be impoverished by the loss of a valuable auxiliary to his business and the problem of finding an adequate substitute for it will not be an easy one to solve.

The blast furnace shown in Fig. 1 has a masonry casing and is typical of the coal-fired furnaces in this plant, although steel casings have been in general use in this country for many years in coal-fired blast-furnace practice. The casing blocks, which may be of masonry or firebrick, are 14 in. thick and are bonded with cement; the structure is strengthened with hoops of  $4\frac{1}{2}$  by  $\frac{3}{4}$ -in. wrought iron. Wire ropes or chains are suspended vertically from top to bottom of the casing to safeguard workmen against injury in the event of the rupturing of the wrought-iron hoops, which occasionally fail. The lower exposed part of the bosh is reinforced similarly with wrought-iron hoops. Commencing above the middle of the bosh, a back lining 2 ft. thick is built between the casing and the lining proper; 4-in. cavities filled with riddled clinker are left between the lining and the back lining and between the back lining and the casing. The plates forming the furnace top are set directly upon the top of the casing but some 9 in. of mine dust is interposed between the plates and the top of the back lining and the lining. The well of the fur-

nace is strengthened with 3-in. thick cast-iron plates bolted around its outer circumference and tied together above the tapping hole with heavy mild-steel straps.

The furnace is 63 ft. 6 in. high, hearth 8 ft. 6 in. dia., bosh 15 ft. 6 in. and throat 12 ft. 6 in. A single bell 8 ft. 6 in. in diameter is used. The furnace has one gas offtake 4 ft. 6 in. in diameter. There are nine  $2\frac{1}{2}$ -in. tuyeres blown with a pressure of 5 lb. per square inch with blast at a temperature of approximately 1250° F. Owing to the position of the massive butts supporting the casing in this type of construction, it is impossible to

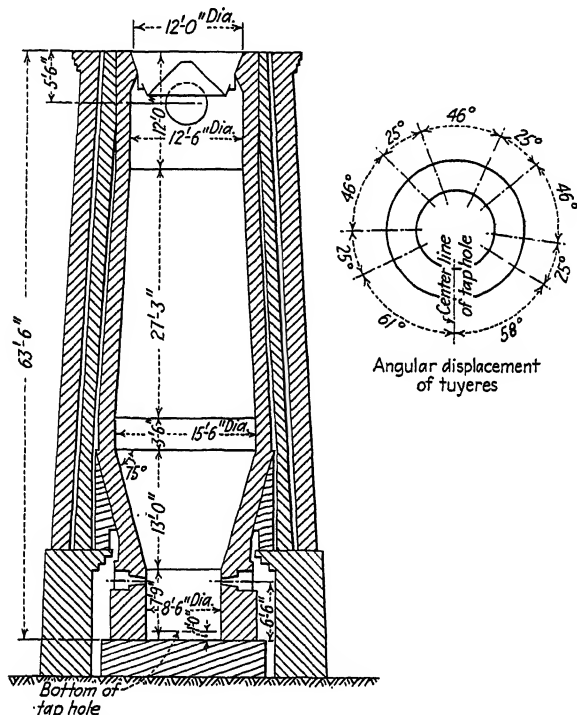


FIG. 1.—SECTION OF COAL-FIRED FURNACE.

obtain a symmetrical arrangement of the tuyeres. Two tuyeres are placed in each of four arches in the casing, which form the tuyere rooms, two on either side of the furnace. The ninth tuyere is the monkey immediately above the tapping hole. The unavoidably narrow wall separating each pair of tuyeres is a weak point in this design. A horse-shoe hot-blast main is employed, the hot-blast inlet to this main being situated at the back of the furnace. The blast for four furnaces is supplied by a single turboblower with a duplicate in reserve. Six regenerative stoves are employed to heat the blast for four furnaces.

Large hand-made blocks have been used for lining the furnace until now, when trials are being made with the view to a change over to the

smaller machine-pressed bricks. Results are not yet available for the latter but a production in the neighborhood of 100,000 tons is looked upon as a satisfactory life for the older type of lining.

In addition to the tuyeres, the only water cooling employed is for the slag notch and the cast-iron lintel plate above it. Jumbos and tuyeres are of the "Scotch" pattern—cast iron cast around a wrought-iron worm tube. The amount of cooling water required is approximately 100 gal. per minute.

This design of furnace may be taken as fairly representative of coal-fired furnaces in this country, although on other plants practically all the details will be more or less modified. Although furnace sizes and outputs have remained more or less stationary, while coke-fired furnace outputs have soared, this is not owing to apathy on the part of the operators of coal-fired furnaces. Efforts to improve the performance of the coal-fired furnace and to obtain larger outputs by departing widely from the lines just described have been uniformly unsuccessful; the low crushing strength of the fuel prevents any furnace of greatly increased dimensions from being successfully operated. Furnaces with larger hearths work slowly and erratically, frequently hang up and generally give a poor performance, accompanied, in our experience, with greatly accelerated wear of the lining. A furnace of 2 ft. greater hearth diameter working on the same burden and fuel and under the same conditions as another of the design described in the foregoing produced 55 lb. of iron per square foot of hearth area per hour while the standard furnace smelted 80 lb. per square foot of hearth area per hour. The fuel consumptions were similar but that of the larger furnace was slightly less than that of the smaller furnace. Similar types of iron were produced by both.

Four charging "doors" are employed in filling the furnace, and each bell carries two barrows of ore dumped at opposite doors and two barrows of fuel dumped at the remaining two doors. The dumping points of the ore and fuel are changed every time the bell is lowered, so that each door receives ore and fuel alternately. The ore is charged by "rounds"; four barrows of ore constitute one round so that at the end of a round each door has received one barrow of fuel and one barrow of ore. This method of rotation of the charges prevents segregation in any vertical section of the furnace. The weight of ore on the barrow depends upon the class of iron being smelted and averages about one ton. The coal barrows carry 15 cwt. and the coke barrows 10 cwt. The stock-line level varies from 12 to 14 ft. and with normal driving the stock descends at the rate of one foot per hour. The furnace is usually cast at 8-hr. intervals and the slag flushed three times between casts.

When splint coals of suitable quality were available the only fuel used in the furnace was coal, except when an old and worn lining was in

use, which was apt to scaffold, when a small proportion of coke was helpful in keeping the stock descending evenly. In recent years, coal of this quality has steadily become scarcer. The ideal fuel is a hard, strong splint, presenting a dull appearance with a few very thin bands of bright coal running through it; No. 1 analysis, Table 1, is of a local

TABLE 1.—*Furnace Coals*

Analysis No.	Composition, Per Cent		
	1	2	3
Moisture.....	10.1	7.3	9.7
Ash.....	4.2	6.2	8.8
Carbon.....	69.0	71.9	67.1
Hydrogen.....	4.7	4.5	4.4
Nitrogen.....	1.3	1.2	1.2
Sulphur.....	0.3	0.6	0.6
Oxygen.....	10.4	8.3	8.2
Volatile matter, less moisture.....	32.8	31.6	27.5
Fixed carbon.....	52.9	54.9	54.0
Calorific value, B.t.u.....	12,120	12,560	11,820

coal of this description. At this plant two rather dissimilar coals are now in use, being charged in roughly equal proportions. The first is a mixed coal consisting of some 60 per cent of a relatively soft bright coal and 40 per cent of a hard cannel coal; No. 2 analysis, Table 1, is of this coal, which when used by itself with a small proportion of coke has given a very creditable performance. The other coal, represented by No. 3 analysis, Table 1, is of a splinty nature, moderately bright in appearance and not hard and strong enough to constitute a first class furnace coal. Used alone its behavior is unsatisfactory—the furnace drives very slowly and irregularly—but when used in the proportions given with the mixed cannel and rough coal plus a small addition of coke, which may be between 5 and 10 per cent, the results are good, a furnace of the dimensions given being then capable of an output of from 320 to 340 tons per week under normal working conditions, and occasionally under exceptional conditions reaching an output of 400 tons in one week's working. The coal is cleaned by hand-picking at the collieries and screened over  $2\frac{1}{2}$ -in. screens; the size of the coal as charged to the furnace is therefore irregular, containing lumps up to one foot or more in size. The presence of a fair proportion of these large lumps does no harm; in fact, their presence appears to be rather helpful. Coals containing dross or carrying too high a proportion of small coal—say up to 4-in. size—are generally found to give less satisfactory results, causing the furnace to drive

slowly and leading to conditions favorable to scaffolding and irregular working.

With a small addition of coke, most bituminous coals will give a reasonable account of themselves in the furnace unless they are unusually weak and friable. The rate of driving does not appear to be appreciably influenced by the amount of volatiles in the coal; that is, coals of lower volatile content do not allow faster driving, as might be anticipated from the lesser amount of tar in the furnace. Experimental work carried out here, using a noncoking semianthracite coal containing 16 per cent of volatiles as fuel proved entirely unsuccessful; this coal was too soft and weak to be really good furnace fuel but its failure was much too complete to be explained by this alone; the absence of the normal amount of tar from the furnace, coupled with the fact that the physical condition of the coal was practically unchanged when it reached the tuyeres, preventing the penetration of the blast, were more probable reasons for its failure. The cannel coal mentioned above is a very hard, strong coal and from this aspect is a most suitable furnace fuel, but while it gives rise to no trouble when used in moderate proportions attempts to run a furnace on this fuel alone proved unsuccessful, again owing to trouble at the tuyeres as the coke yielded by this coal is extremely dense, nonporous and

TABLE 2.—*Calcined Ironstones*

Analysis No.	Composition, Per Cent					
	1	2	3	4	5	6
Iron.....	58.7	54.4	48.6	50.2	50.6	51.4
Silica.....	4.3	3.6	17.1	10.9	14.5	8.2
Alumina.....	0.4	1.2	0.6	5.1	8.2	6.6
Lime.....	3.7	3.4	1.1	4.4	2.5	5.5
Magnesia.....	4.7	8.3	1.6	2.3	1.1	3.6
Phosphorus.....	0.64	0.53	0.48	0.57	0.43	1.10
Manganese.....	0.95	0.98	0.63	1.13	0.62	0.79
Sulphur.....	0.50	0.41	0.25	0.40	0.23	0.16

resistant to blast penetration. Our general experience is that, provided the coal is of suitable physical character, its performance in the furnace will be fairly closely in line with its calorific value except in the case of a coal of high volatile content, when the consumption figure will be high.

The small proportion of coke charged with the coal does not rob the pig iron of any of the desirable qualities always associated with coal-smelted iron, presumably because the volume of tar yielded by the large proportion of coal still used is quite sufficient to maintain the same conditions as prevail in the all-coal-fired furnace, and because the rate of meltings is not unduly accelerated, this, under average conditions,

being in the neighborhood of 75 lb. of iron per square foot of hearth area per hour.

Up to some 20 years ago, the burden at this plant consisted of 50 to 75 per cent of locally mined clayband and blackband ironstones, which are calcined before being charged into the furnace. The balance of the burden was made up of easily smelted Cumberland and Spanish ores of low phosphorus and manganese content. Although local ironstones are still available, if not so plentiful as they once were, the question of cost, coupled with the difficulties in obtaining supplies, has led to their being partly replaced by imported ores. At this plant, with every endeavor being constantly made to augment the quantity available, the average consumption of ironstones has dropped to 20 per cent of the total ores used.

In Table 2 representative analyses of a few of these ironstones are given; the analyses noted do not by any means exhaust the variety of these materials available. As a rule, the phosphorus contents are high and it is unusual to find an ironstone with less than 0.1 per cent of this element; the manganese content may vary between 0.3 and 3 per cent. A loss of from 25 to 40 per cent occurs during the process of calcination. The amount of sulphur in the raw stone varies from a trace upwards; the sulphur content of the calcined stone will depend largely upon the method employed in and upon the control of the calcination process. Calcination in kilns is more effective in reducing the sulphur content than is calcination on hearths.

The ironstones are very easily smelted and form an ideal burden for the coal-fired furnace; when the alumina content is low enough to allow a free-running slag to be formed they have the tendency to simplify the production of low-silicon, low-carbon pig iron.

The choice of ores to supplement or replace the local ironstones is restricted by the capabilities of the fuel. Dense magnetic ores are troublesome and their use leads to high fuel consumption accompanied by the appearance of symptoms of indigestion in the furnace. Their use is therefore avoided if at all possible. Some of the more refractory types of hematite ores have also to be avoided for the same reasons. All ores used are almost invariably charged as mined. Magnetites are an exception but even when crushed to 4 to 6-in. size they are difficult to smelt. After calcination the only preparation the ironstones receive is that of screening out the dust.

The problems confronting the furnaceman operating a coal-fired furnace are similar in nature to his neighbor's on a coke-fired furnace, if we except any worries connected with the operation of charging equipment that is unnecessary for the smaller furnace. Owing to the slow rate of travel of the stock, scaffolding is probably rather more prevalent. Those scaffolds are sometimes overcome after a few hours

by the furnace itself, charging in the interval being confined to "patching" in the deep door or doors. Tuyeres are sometimes adjusted to direct the working of the furnace against the obstruction and in obstinate cases at this plant the furnace is blown down until the location of the scaffold is reached and a fuel blank charged to melt it off; this treatment is invariably effective. Towards the end of a long campaign breakouts sometimes occur if the well of the furnace has become badly eroded. The well plates do not offer the same safeguard against this form of trouble as do the strong well jackets of furnaces of modern design. Furnaces that have broken out through brickwork and well plates, however, have been patched and successfully run for long periods afterwards.

Six men are required to man each furnace: one bellman, two fillers and a weighman on the furnace bank and a keeper and his assistant on the foreshed. This crew is augmented when the furnace is being cast and in the times of trouble that are inevitable on a blast-furnace plant. The pig iron is cast in sand pig beds and loaded by hand; at the stock benches it is broken by hand before stacking.

TABLE 3.—*Analyses of Shotts Pig Iron*

	Composition, Per Cent				
	3 Soft	4 Soft	Cylinder (4 Hard)	Low Phosphorus (3 Soft)	Special (4 Hard)
Silicon.....	2.8	1.8	1.50	2.5	1.70
Sulphur.....	0.03	0.06	0.09	0.03	0.08
Phosphorus.....	0.60	0.50	0.35	0.14	0.30
Manganese.....	1.2	1.0	0.85	0.85	1.0
Graphitic carbon.....	3.40	3.10	2.65	3.30	2.10
Combined carbon.....	0.25	0.45	0.67	0.40	0.75

Specimen analyses of some of the pig irons produced are given in Table 3. The iron is graded into the following range of fractures: No. 1, No. 3 Soft, No. 3 Medium, No. 3 Hard, No. 4 Soft, No. 4 Hard, Mottled and White. The first three analyses represent normal coal-smelted pig iron smelted from burdens containing a moderate proportion of local ironstones. The low-phosphorus pig iron is smelted from a burden carrying no local ironstone. Silicon contents of the gray irons may range from 0.5 to 6 per cent; sulphur from a trace up to 0.12 per cent in the very hard grades and up to 0.3 per cent in white iron; phosphorus ranges from 0.15 to 1.5 per cent; manganese from 0.3 to 2.5 per cent; the total carbon in soft irons is around 3.5 to 3.75 per cent and in hard cylinder qualities from 3.0 to 3.3 per cent. The last analysis given, included as a matter of interest, is an unusual one for direct furnace metal and is not an iron for which the furnace can be deliberately

burdened; it is the product of an irregularly working furnace with one or perhaps two doors driving slightly faster than the others. Fuel consumption is rather high under these conditions and the slag, although not the black ferrous silicate slag of a furnace in trouble, carries a higher amount of iron than is normal. It would appear to be the outcome of incompletely reduced material arriving in the well of the furnace where its reduction is completed partly at the expense of some of the carbon in the metal in the well. It is an extremely strong and tough metal with good casting properties and carries its strength and toughness into the castings made from it.

Slag volumes vary with the type of iron being smelted and with the burdens used and range from 8 to 14 cwt. per ton of pig iron. An average analysis of the slag will be:  $\text{SiO}_2$ , 32.0 per cent;  $\text{Al}_2\text{O}_3$ , 17.0;  $\text{FeO}$ , 0.6;  $\text{CaO}$ , 43.5;  $\text{MgO}$ , 3.5; S, 1.6. The alumina content may rise to 25 per cent on occasion, but this type of slag is more viscous than is desirable and also has the effect of making it difficult to produce low-silicon irons.

Over a four months period with two furnaces in blast during three months and three furnaces in blast during the last month of the period, the output of pig iron was 13,026 tons. The coke used varied from nil to 8.5 per cent, the average over the period being 5.3 per cent. The fuel consumption in terms of coal—taking two parts of coke as equivalent to three parts of coal—averaged 30.1 cwt. per ton of pig iron: the actual figures are 1.54 cwt. of coke and 27.74 cwt. of coal. The pig iron smelted consisted of almost equal proportions of 3 per cent silicon soft iron and 2 per cent silicon hard iron. The consumption of limestone—52 per cent total lime, fluxing efficiency 50 per cent—averaged 9.3 cwt. per ton of pig iron. The amount of gas made—metered on leaving the by-product plant and therefore exclusive of losses—was 168,000 cu. ft. per ton of pig iron. Of this gas, 38 per cent was used in the hot-blast stoves, 45 per cent in the furnace boiler plant raising steam for power, 14.5 per cent in the by-product boiler plant raising steam for power and process work and 2.5 per cent at the tar stills. The average gas analysis was:  $\text{CO}_2$ , 7.7 per cent;  $\text{O}_2$ , 1.8;  $\text{CO}$ , 27.0;  $\text{CH}_4$ , 2.1;  $\text{H}_2$ , 5.7;  $\text{N}_2$ , 55.7; calorific value, 134 b.t.u. per cubic foot.

The furnace gases pass through condensers, washers and scrubbers, where tar and ammonia are extracted. Some 15 lb. of dry, neutral sulphate of ammonia is recovered per ton of coal used. The tar on distillation in the old type of pot still yields, per ton of coal, about  $3\frac{1}{2}$  gal. of virgin blast-furnace creosote oil containing 35 per cent phenols and about 120 lb. of medium soft pitch with an ash content of about 8 per cent. When rapidly distilled in a modern continuous still in an atmosphere of steam, the oil yield is increased to over 8 gal. with 30 per cent phenols and the yield of higher ash pitch correspondingly reduced.



## DISCUSSION

*(R. M. Marshall presiding)*

H. CLARKE,\* Springville, Ala. (written discussion).—Much of the ore in the coal-burning furnace, according to Mr. Allan, is impregnated with carbon. Of course, we would expect the intimate association of the reducing agent with the ore to promote reduction. But in the reduction of ores, I do not think much, if any, attention has been paid to the important role carbonaceous matter might be made to play, not as a reducing agent, but as an agent for virtually raising the melting temperatures of some ores.

But why raise their melting temperatures? Simply because the body of coke in a blast furnace will not support a liquid; liquid ore, in its rapid passage through the incandescent coke, is denied the time necessary for thorough reduction.

At its temperature of reduction, iron ore is a solid; at their respective temperatures of reduction, both the oxides of manganese and silicon are usually constituents of liquid slags. These properties doubtless largely account for the fact that the average blast furnace is close to 99 per cent efficient as a producer of iron; as a producer of manganese, it is less than 70 per cent efficient; as a producer of silicon, it is perhaps the industrial world's worst performer.

So it appears that what is needed in the blast furnace for more complete reduction are manganese ore and siliceous materials that will behave like solids at their temperatures of reduction. For filling this need, use of carbon immediately presents itself as a possibility because we know that the so-called carbonaceous deposits in blast furnaces have extremely high melting temperatures in spite of being composed largely of oxide combinations with rather low melting points.

Some experiments carried out in the Research Department of Crane Enamelware Co. throw considerable light on properties of slags mixed with carbonaceous matter. I believe these experiments show the way to more complete reduction of manganese and silicon in the blast furnace and perhaps the way to better performing pig iron.

These experiments revealed that the addition of finely pulverized charcoal or coke had little effect on the properties of siliceous slags containing no heavy metals. When such slags were mixed with these carbonaceous materials and brought to a high temperature, much of the coke or charcoal was expelled soon after the slags changed to the liquid state. Apparently coke and charcoal do not possess the property of wetting molten siliceous matter.

It was found that coking coal will wet molten siliceous matter; apparently for that reason, addition of coking coal will greatly modify some of the properties of slags. For example, we show two mixtures of pulverized materials with some of their properties:

100 parts glass cullet	}	All of this mixture was changed to a homogeneous liquid with the consistency of thin sirup at 2445° F.
15 parts fluorspar		
15 parts borax		
100 parts glass cullet	}	Sixty-five per cent of this mixture was not melted at 2445° F., 20 per cent was apparently solid at 2745°.
15 parts fluorspar		
15 parts borax		
10 parts coking coal		

Fig. 2 essentially illustrates the behavior of pulverized manganese ore alone and mixed with two forms of carbonaceous matter. This ore showed about 3 per cent of iron and 42 per cent of manganese, mostly in the form of  $MnO_2$ . The behavior of this ore was in many respects identical with the behavior of the slag just described.

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\* Acheson-Clarke Co.

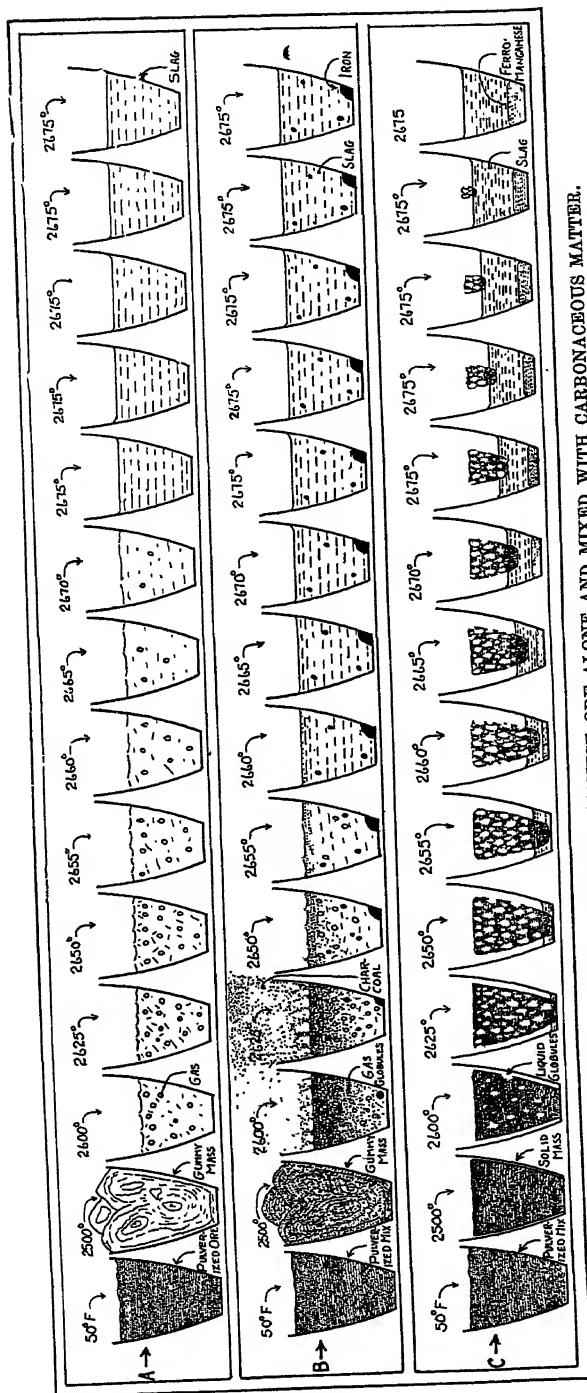


FIG. 2.—BEHAVIOR OF PULVERIZED MANGANESE ORE ALONE AND MIXED WITH CARBONACEOUS MATTER.

- a, pulverized manganese ore.  
 b, mixture 70 per cent manganese ore, 30 per cent charcoal.  
 c, mixture 70 per cent manganese ore, 30 per cent coking coal.

Figs. 2a show manganese ore alone. At 2500° F. it changed to a swelling gummy mass; from 2600° to 2650° it was a vigorously boiling, viscous liquid. After the boiling period, at about 2660°, the liquid had the consistency of fairly thin sirup; its viscosity decreased with rising temperature.

Fig. 2b shows the behavior of an intimate mixture of 70 per cent of the same ore and 30 per cent charcoal ground to 200 mesh. When the temperature reached 2600°,

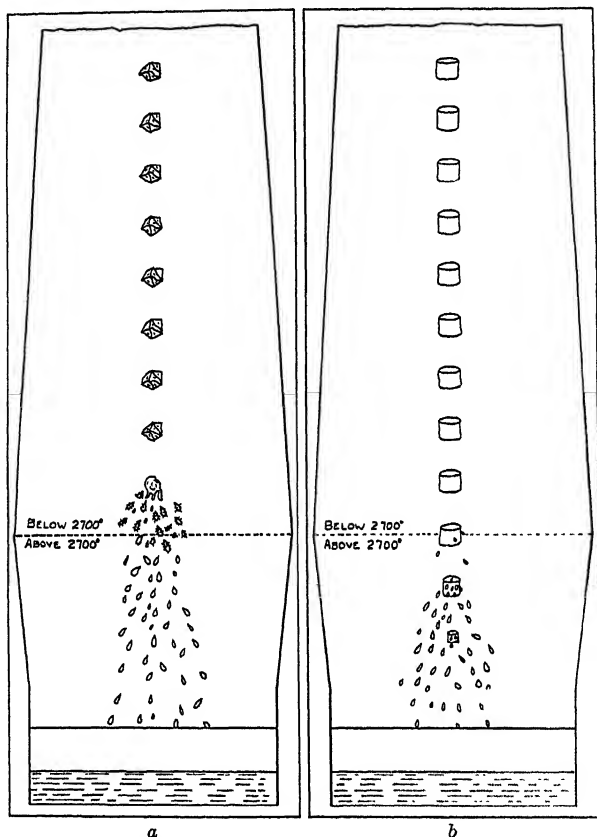


FIG. 3.—BEHAVIOR OF MANGANESE ORE IN BLAST FURNACE.  
a, manganese ore alone.  
b, briquetted mixture of coking coal and manganese ore.

the charcoal began to separate itself from the ore; at 2665° apparently most of the charcoal had escaped. Contents of the crucible yielded a few tiny particles of magnetic metal equal to about 5 per cent of the metallic content of the ore.

Fig. 2c shows the behavior of a mixture of 70 per cent of the same ore with 30 per cent coking coal. This mixture possessed the properties of a solid mass at temperatures well above the melting point of the ore. The mixture failed entirely to pass through the gummy state; it passed directly from a solid to a thin liquid. The sweating continued over a period of more than 45 min. At the end of the heat, the crucible contained a pellet of ferromanganese with a weight equal to 32 per cent of the weight of the metal in the ore.

The laboratory experiments described enable us to predict the behavior in the blast furnace of manganese ore and the same ore mixed with coking coal and made into

briquettes. Fig. 3a shows the ore behaving very much as it behaved in the crucibles; it first becomes gummy; then it melts; it then yields oxygen, after which it changes into a thin liquid, which, of course, trickles rapidly through the incandescent coke.

Fig. 3b shows a briquetted mixture of manganese ore and coking coal behaving as the same mixture behaved in the crucible. The ore doubtless remains in the high-temperature zone long enough for quite thorough reduction.

Reduction of manganese could be further promoted by the presence in the briquette itself of strongly basic influences.

The reduction of silicon could be promoted by an acid condition in the briquette; also by immediately available iron from iron ore in the briquetted mixture.

As the result of smelting briquettes made of pulverized manganese ore and coking coal in an ordinary foundry cupola, we have already obtained what we consider to be a fairly reliable index of what they would do in a blast furnace. By charging these briquettes into the cold blast cupola while melting iron for castings, we have repeatedly recovered over 55 per cent of the manganese in the ore. Considering the "drop" in manganese due to oxidation, we estimate that the actual recovery was over 70 per cent. This recovery was obtained in spite of strongly acid slags.

Cupola charges made up only of briquettes, coke and a little limestone yielded an alloy that analyzed 40 per cent manganese and 14.7 per cent silicon. The briquettes were made with manganese ore and coal; low manganese yield was most likely due to absence of basic slag. The 14.7 per cent silicon, it should be noted, was obtained in spite of low temperatures and in spite of the oxidizing atmosphere which doubtless existed in the cupola. This alloy was unexpected; we obtained it while attempting to make a slag rich in manganese oxide.

The briquetted mixtures I have described carry their own "reducing atmosphere," the ores have immediately available enough reducing agent for complete reduction. Their "own reducing atmosphere" makes possible reduction in the presence of furnace gases which are not necessarily reducing; immediate availability of the reducing agent makes slow reduction by gases in tall stacks unnecessary.

It must be admitted that use of the coal-ore briquettes is not yet out of the experimental stage. Nevertheless, we feel that they have advanced us a few steps, toward the new blast furnace that burns its own carbon monoxide and does all its reducing a few feet above the tuyeres. Such a furnace would have no stoves; it would have upper tuyeres; its blast pressure would be less than 3 lb., and it would be a little taller than the average foundry cupola.

Now getting to the uses of the briquetted mixtures for silicon and manganese reduction in the standard blast furnace, particularly in the Birmingham district where large quantities of highly siliceous iron ores are available and where the practice of adding manganese ore to the furnace burden is almost general: Production in furnaces on foundry iron could be appreciably increased by switching from the present method of using additional coke for increasing silicon to a method involving the simple addition of briquetted mixtures of coal and siliceous iron ore. Some evidence points to incomplete reduction of manganese ore as the cause of poor performance by pig iron. If this is true, then briquetted mixtures of coal, manganese ore and lime offer an economical way to make iron that should approach, if not excel, the quality of coal-smelted pig iron.

## Blast-furnace Practice in France

BY F. CLERF,\* MEMBER A.I.M.E.

(Birmingham Meeting, April, 1937)

BLAST-FURNACE practice in France is determined more or less by the character of the ores used. Some French ores are siliceous and others are calcareous, therefore by proper burdening a self-fluxing mix can be used. This is not always done, as, for instance, at the Caen furnaces of the Société Métallurgique de Normandie, where the Soumont ore of Normandy is used, which is a carbonate. This ore is crushed and calcined at the mines, yielding a product that is porous and well sized for blast-furnace consumption.

The lines of the Caen furnaces are given in Fig. 1. Originally these furnaces had 16 tuyeres; six are plucked and these tuyeres are set in the lower part of the bosh. Operating data on these furnaces are given in Table 1.

TABLE 1.—*Operating Data, Caen Furnaces*

	Kg.	Lb.
Blast-furnace burden per ton of iron:		
Soumont ore.....	2000-2100	(4400-4650)
Limestone.....	900-1000	(2000-2200)
Basic Bessemer slag (bearing phosphorus).....	100	(220)
Scale.....	35	(77)
Manganese ores.....		
Coke.....	1100-1200	(2420-2640)
Coke analysis: Ash, per cent.....	9.5	
H <sub>2</sub> O, per cent.....	4.0-10.0	
Flue dust (approx.), kg. per metric ton....	200	(440 lb.)
Blast volume, cu. m. per hr.....	83,000	(49,000 cu. ft. per min.)
Pressure, lb.....	12	
Blast heat, deg. C.....	650	(1200° F.)
Top temperature, deg. C.....	250	(445° F.)
Top-gas analysis, per cent.....	CO <sub>2</sub> 9.3	CO 30.3
	O <sub>2</sub> 0.3	H <sub>2</sub> 3.0
Production per 24 hr. about 510 tons.		

### MINETTE ORES

The most important ore deposits in France are in the west of Lorraine. They are called the "minette" ores and are of two classes—siliceous and

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calcareous. The behavior of these ores in the furnace may be different, and from this point of view, classed as follows: (1) those exploding when heated rapidly, (2) those behaving without explosion on the same test. In the first ores the moisture in the interior of the pieces cannot escape and causes the pieces to break up, giving off a great amount of dust. It has been demonstrated, in small-scale and large-scale experiments, that the blast-furnace smelting is favorably influenced when the lumps are broken to approximately 3 in. The iron is better both physically and chemically. Gas analyses reveal a slightly increased indirect reduction and a decrease in coke consumption. However, a greater amount of flue dust is produced, which builds up in the bosh, and after a few weeks difficulties arise in operation.

One method of overcoming these difficulties is to put in a second row of tuyeres, called emergency or auxiliary tuyeres, to smelt away the scaffolds, thereby keeping the bosh clean and permitting the furnace to move. One very modern plant has installed three rows of tuyeres, two in the bosh. This practice was considered absolutely necessary to keep the furnace in operation, but it necessitates a higher coke consumption and the quality of the iron is apt to be affected.

In the early days of hand-charging furnaces, it was common practice to break the large lumps into pieces with a hammer. With the introduction of mechanical charging, this practice was abandoned, and no ore preparation was done for a number of years. But, following a general trend in the steel industry not only to solve engineering problems but also metallurgical questions, blast-furnace men after the war again investigated the advantages to be derived from a uniform burden, both chemically and physically. The problem has not found a definite solution in the eastern French blast furnaces and the question is still open even today as to whether or not it is advantageous to prepare the blast-furnace burden when using minette ores.

The iron works of Volklingen (Sarre), owned by Mr. Rochling, have pioneered work in the field of preparation of the burden. Since the war, the Sarre works have been compelled to buy all their ores in Lorraine. The works of Volklingen have bought most of the dust accumulated before and since the war in the neighborhood of the blast furnaces. The

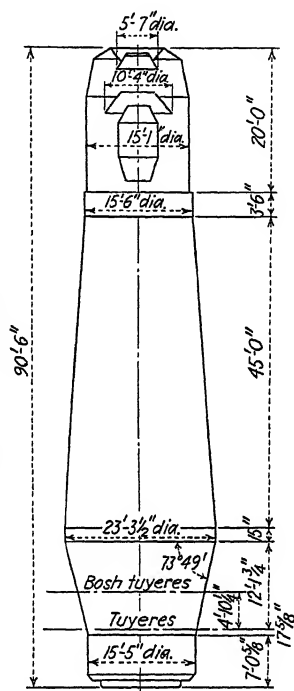


FIG. 1.—LINES OF BLAST FURNACES AT CAEN.

TABLE 2.—*Results of Operation at Sarre Works\**

	Analysis, Per Cent	Coke Consumed, Kg.	Yield, Per Cent	Materials Smelted, Per Cent	Flue Dust, Kg. per Ton of Iron
Basic Thomas pig iron	0.3 Si 1.0 Mn 1.9 P 0.07 S	898	38.3	59 sinter 34 minette ore crushed and screened 2.9 manganese ores, not pre- pared 1.3 scrap 1.3 scale 1.5 miscellaneous	25
Basic Thomas pig iron	0.25 Si 0.9 Mn 1.8 P 0.08 S	875	38.2	53.5 sinter 37.0 minette ore (not pre- pared) 2.9 manganese ores 1.6 scrap 3.2 scale 1.8 miscellaneous	35
Basic Thomas pig iron	0.3 Si 1.05 Mn 1.9 P 0.07 S	863	39.8	57 sinter 30.8 minette ore 2.4 manganese ore 3.6 scrap 2.6 scale 3.6 miscellaneous	32
Hematite pig iron (Stahleisen)	0.8 Si 4.8 Mn 0.11 P 0.026 S	812 <sup>b</sup>	51.4	39 sinter 18 foreign ore (crushed, not screened) 11 scale 8 manganese ore (not pre- pared) 4 cinder from Fe-Mn blast furnace 6 scrap 14 limestone (crushed and screened)	
Foundry iron	2.5 Si 1.0 Mn 0.09 P 0.032 S	1018	46.2	35 Spanish carbonate, crushed, not screened 15 Spanish carbonate, raw 5 sinter 6 red hematite (crushed, not screened) 8 scale 10 scrap iron 21 limestone	
Foundry iron with phosphorus from minettes	2.8 Si 0.8 Mn 1.6 P 0.019 S	1036	38.6	20 sinter 75 minette ore (crushed and screened) 1 scale 4 scrap iron	

\* A. Wagner: *Stahl und Eisen* (Feb., 1931) No. 8.<sup>b</sup> Coke 10 per cent ash and 8 per cent moisture.

dust was considered of no value, except for the price of loading into railway cars. Thus these furnaces use a burden with about 30 to 50 per cent flue dust, containing 40 per cent Fe, and the remainder minette

ores. The ores are crushed, screened, and the fines sintered with the flue dust in a large Dwight-Lloyd plant; making a uniform burden available for the blast furnaces. A description of the plant, equipment and ores used has been given in *Stahl und Eisen* (Feb., 1931, No. 8) by A. Wagner, blast-furnace superintendent. He does not mention the duration of time over which the results were obtained. The results as given in that description are shown in Table 2.

From the first tests of crushing in 1925 to when the large Dwight-Lloyd plant was completed and put in operation in 1930, the coke consumption per ton of iron has decreased from 1350 to 900 kg. and the output of iron has increased from 170 tons to 270 tons in the same stack, of 500 cu. m. volume and 13-ft. 6-in. hearth diameter.

Crushing, screening and ore preparation in general have not found favor in other plants in spite of the remarkable figures and results obtained at Volklingen and Neunkirchen. This may be explained by the fact that the years following 1931 have been years of deep depression in the French steel industry. The price of coke decreased from 120 francs a ton in 1931 to 75 francs in 1936 before June, or \$8 in 1931 and \$5 in the early months of 1936. The ratio of decrease is thus  $\frac{8-5}{8} = 37$

per cent. All the works are quite careful of their blast-furnace gas as a metallurgical fuel, and the production of pig iron being only 50 to 60 per cent of the production in 1931, there was scarcely enough for heating and generating electricity. Therefore, any decrease in the consumption of fuel would have led to difficulties in the thermal balance of the plant. It seems that under present conditions the benefit of crushing and screening ores and sintering fines would be very small, if any.

It must be said that all attempts to drive hard furnaces with minette ores have always failed because of the excessive amount of flue dust produced. Until 10 or 12 years ago, standard practice was to produce from 150 to 200 tons per day in furnaces of about 500 to 600 cu. m. capacity. Attempts to blow more blast have always led to 250 or 300 kg. of flue dust per ton of pig iron; and in some instances 450 kg. of flue dust per ton of iron was experienced when production of iron went from 350 to 400 tons per day.

Except for slow blowing, as it has been practiced everywhere during the depression period, there has been nothing done of much interest. One characteristic of the steel plants of Lorraine and Luxemburg was to have relatively small daily outputs per furnace, but a great many stacks in operation. Therefore, to adjust the pig-iron production to the need of the plant was more a question of blowing a small or large number of units than of modifying the practice in any of them.

As far as I know, no general information on French blast-furnace practice has been published in nine years. Unfortunately, we do



not have committees in France as they exist in Germany, England or the United States. There is little intercourse between the different plants or exchange of ideas and results obtained. A good paper on the subject was read in Luxemburg in 1927 and is still of interest because most of the French plants have made very few alterations on their blast furnaces; and a summary is given below.

### FURNACE LINES AND OPERATION

Figs. 2 to 13 show the lines of several furnaces from different plants, and Table 3 gives a good average of Luxemburg and Lorraine blast-

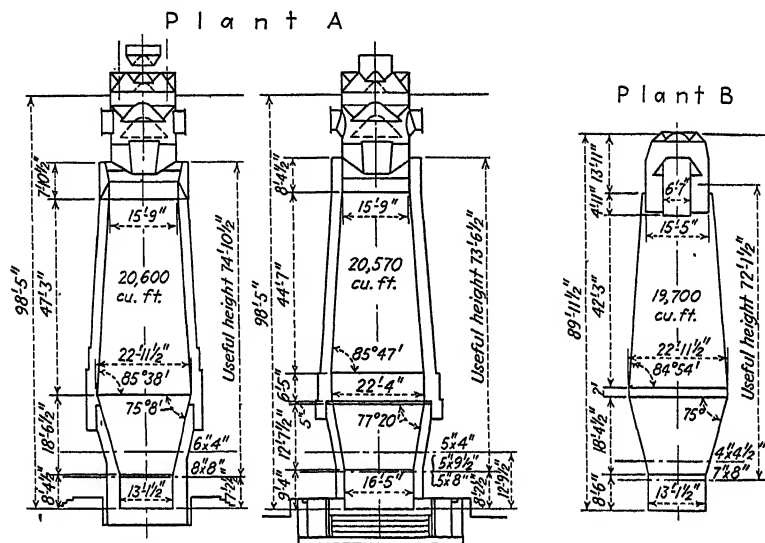


FIG. 2.

FIG. 3.

FIG. 4.

FIGS. 2-4.—LINES OF LORRAINE-LUXEMBURG BLAST FURNACES.

furnace results. The coke consumption also is given in the table. It lies around 1000 to 1025 kg. of coke for one ton of pig iron with a yield of 31 to 32 per cent in average good practice and with 25 to 30 kg. of coke more or less for one point of yield less or more.

Blast-furnace lines have been altered slowly and changes made in the same direction as in American furnaces. In one plant the hearth has been enlarged 4 ft. and the bosh lowered 3 ft. in 27 years. It must be said that furnace campaigns lasted from 15 to 20 years, owing to slow driving, and few opportunities were offered for rebuilding.

Generally there are eight tuyeres, 7 to 9 in. in diameter. Bosh tuyeres are 5 to 6 ft. above the row of main tuyeres.

The stacks are banded like the bosh in American furnaces and the top and charging apparatus rest on heavy columns, giving blast-furnace plants a peculiar appearance. I know of only two companies that have

had their furnaces built by American engineers; the first in 1910 and the other in 1929 and 1930. These furnaces are skip-filled while the others are bucket-filled.

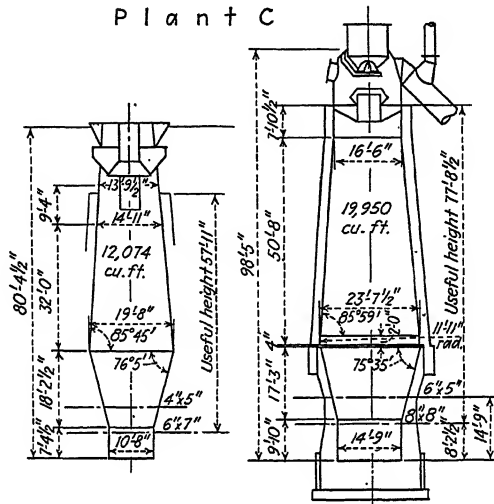


FIG. 5.

FIG. 6.

FIGS. 5 AND 6.—LINES OF LORRAINE-LUXEMBURG BLAST FURNACES.

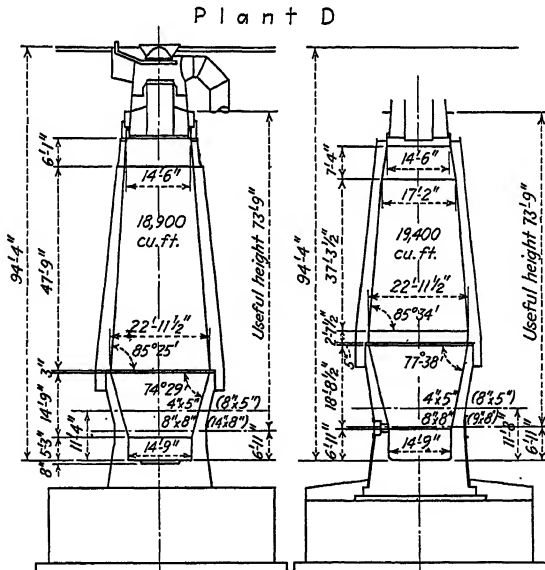


FIG. 7.

FIG. 8.

FIGS. 7 AND 8.—LINES OF LORRAINE-LUXEMBURG BLAST FURNACES.

The furnaces are generally blown by pressure and all blowing engines blow in the same main. Blast heats are high, from 750° to 800° C.,



and it is claimed that the power consumption has been reduced by 25 to 30 per cent in comparison with the older types of disintegrators.

The wet cleaning systems all depend on intimate mixing of gas and water, first in a static scrubber and then in fan disintegrators. The cleaned gas obtained is thus perfectly cool and contains a minimum of

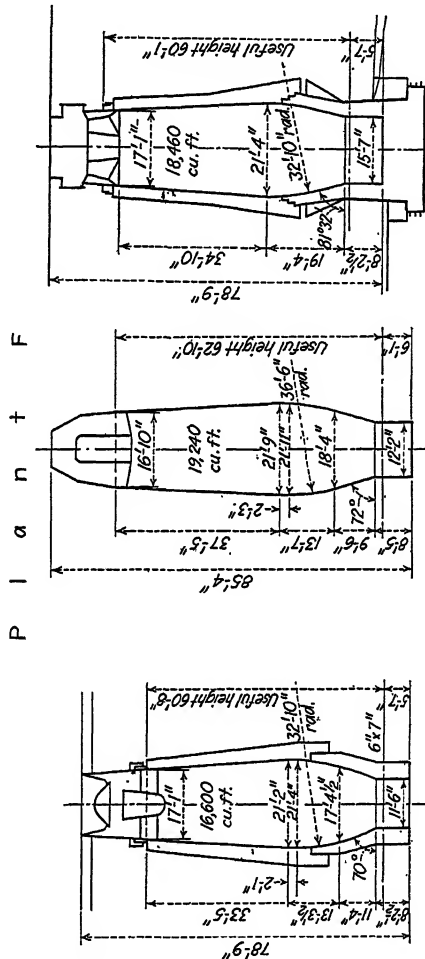


FIG. 13.

FIG. 12.

FIG. 11.

FIGS. 11-13.—LINES OF LORRAINE-LUXEMBURG BLAST FURNACES.

moisture. The disintegrator requires a large amount of power, three or four times as much as in the Halberg-Beth system.

Clean blast-furnace gas is a vital requirement in the use of gas-driven blowing engines, gas-driven power engines and modern stove practice. A cleanliness of 0.02 grains per cu. m. is necessary for gas engines and 0.02 to 0.05 for stoves with small checkers. Gas-driven blowing engines have proved to be very well adapted for blast-furnace plants and their reliability and great economy as obtained in installations

TABLE 3.—Operating Data, Lorraine-Luxemburg Furnaces

Plant	A			B			C			D		E			F		
	2	2	3	4	4	4	5	6	7	8	9	10	11	12	13		
Furnace, Fig. No.																	
Put in blast, year.....	1911		1927	1912	1912	1912	1910	1920	1920-23	1926		1925					
Relation: $\frac{\text{bosh dia.}}{\text{hearth dia.}}$ .....	1.75	1.75	1.36	1.75	1.75	1.75	2.0	1.56	1.55	1.55	1.82	1.53	1.85	1.80	1.37		
Relation: $\frac{\text{top dia.}}{\text{hearth dia.}}$ .....	1.20	1.20	0.96	1.18	1.18	1.18	1.53	1.13	0.98	0.98	1.31	1.07	1.48	1.40	1.07		
Average blast pressure, lb.																	
per sq. in. ....	8	9.65	10.8	6-6.16	5.6	6.57	4.4-5.4	7-8.7	10.8	11.6	6.16-6.57	5.4-6.37	4.2	5.2			
Production in 24 hr. <sup>a</sup> tons ...	246	306	342	229	241	281	150	300	300	304	135	220	157	223			
Yield of burden, per cent. ....	29.4	26.6	25.7	27.16	27.85	26.81	27	27	28.3	28.0	26-32	26.05	27.09	27.09			
Flue dust per ton iron, lb. ....	289	458	516	237	121	242	352	300	641	890	368	315	77	83			
Coke per ton ore, lb. ....	685	683	657	714	811	725	774	701	718	696	852	703	698	720			
Blast heat, deg. Cels. ....	817	771	780	830	868	814	700	650	680	650	710	765	815	740			
Average time of descent of charges.....	19.30	14.21	12.30	18.09	16.34	14.29	16.23	17.36	13.49	13.54	19.29	17.44	22.43	18.03			
Coke burned in hearth 24 hr./m. <sup>-1</sup> t. ....	20.70	28.60	20.70	21.70	25.40	27.50	23.20	18.60	21.7	22.03	20.70	18.50	19.20	25.20			

<sup>a</sup> This production is not a monthly average, but an average of the days when there is no hanging.

built in the light of the latest experience is now a well established fact. Units as large as 4000 to 5000 hp. have been built with two gas cylinders and one air cylinder, and are sufficient to blow furnaces to 500 to 600 tons output a day, with a gas consumption of less than 2.5 cu. m. gas per horsepower.

### THE DENAIN PLANT

The steel industry in northern France dates back to the beginning of the last century and has been established in the vicinity of the northern coal fields. The reasons for this are obvious, as cheap coal was the principal requirement of any industry, and in fact most of the French factories were located in the north of France. Glass factories, steel and iron foundries, locomotive and rail-material factories, spring, bolt and nut factories, heavy forging, etc., all are concentrated in the vicinity of cheap coal, with best conditions for good labor.

The first blast furnaces depended on foreign ores, but at the end of the last century, the Thomas basic Bessemer process was introduced for all common steels. The ores are shipped from Lorraine over a distance of about 150 miles, and although pig iron is cheaper to produce in Lorraine, there remains an advantage for the northern steel mills through the fact that most of the large consumers are near the mills and consumption is superior to the production of northern steelworks.

Our company has always specialized in the manufacture of heavy and medium plates, and also of all qualities of steel for forging, pressing, tubes, etc. All of these qualities, naturally, depend on the basic open-hearth furnace or the electric furnace, but we also manufacture Thomas basic steels in sheet bars, merchant bars, etc. We have four blast furnaces, two on basic Bessemer iron, one on special grades, foundry, stahleisen, etc.

Until the year 1931, the relative quantities of Thomas steel and open-hearth steel was as 60 to 40, but open-hearth steel has prevailed since that time. The necessary basic Bessemer pig iron has always been produced in two furnaces, and the output, which was 27,000 or 28,000 tons per month in 1930, has dropped to 12,000 tons in some months of exceptional depression. The operating conditions of these extremes are given in Tables 4 to 7.

Our company owns ore mines in the west of France, south of Caen, and in eastern France, both siliceous and calcareous ores. We also have a Greenawalt sintering plant with three pans of standard dimensions, and operate two of them, so that a relatively large part of the burden is composed of sintered material.

Our furnaces (Fig. 14) were rebuilt in the years 1928 and 1931, having the lines represented on Figs. 16 to 18. I have incorporated American design in every possible detail and am indebted to American blast-

furnace men, from whom I have always received the greatest courtesy and help. Besides, modern European practice has developed by following American pioneering footsteps.

TABLE 4.—*Typical Blast-furnace Burden for Basic Thomas Pig Iron*

	Rapid Driving, 1930	Slow Driving, April, 1934	At Present (Jan., 1936)
	Kg.	Kg.	Kg.
Normandy siliceous ore.....	394.8	303.4	336.1
Siliceous minette.....	817.4	137.7	
Calcareous minette (from 30 to 31 per cent Fe).....	1715.2		
A.....		837.4	922.8
B.....		713	590.0
Manganese ores.....	41.4	10.2	22.4
Open-hearth slag.....	175.1	242.3	146.6
Cinder: from reheating furnaces...	3.7	3.3	5
From rolling mill.....		59.2	20.9
Sinter (pyrites, cinder and flue dust)	300.7	426.9	472.3
Miscellaneous scraps.....	52.3	35.2	145.2
Fine iron separated by magnet from converter spittings.....	38.5	18.2	14.2
Lime phosphate.....		20	31
Limestone.....			5.5
Total burden per ton iron.....	3539.1	2806.8	2712
Production in 24 hr. (several months average), tons <sup>a</sup> .....	464.8	263.4	352.8
Flue dust per ton of iron, kg.....	290	100.1	175.6
Coke consumption per ton of iron, kg.....	1135.7	966.6	861.9
Burden yield, per cent.....	28.3	35.6	36.9
Volume of blast as given by daily reports:			
Per metric ton of iron, cu. m..	3609	3045	2715
	(127,400 cu. ft.)	(107,500 cu. ft.)	(95,800 cu. ft.)
Per hour, cu. m.....	69,000	33,400	39,900
Per minute, cu. ft.....	42,000	20,000	23,760
Heat of blast, deg. C.....	630	644	649
Temperature at top, deg. C.....	162	175	193

<sup>a</sup> The highest monthly output has been 16,000 tons of basic pig iron.

Since the use of more sintered material with pyrite cinder, and especially since the time of slow blowing with periods of fanning, we have experienced some trouble due to the growing of the stack. According to European continental construction, our stacks are not enclosed by a heavy shell, but with heavy bands. The top of the furnace is supported by heavy columns, also according to Continental practice. A

TABLE 5.—*Analyses of Burden*  
ANALYSES, FEBRUARY, 1930, PER CENT

	Al <sub>2</sub> O <sub>3</sub>		CaO		MgO		Fe		Mn		S		P		Mole- ture		
	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet			
Normandy siliceous ore.....	12.9	12.7	9.6	9.4	2.3	2.3	1.3	1.3	44.6	44	0.4	0.4	0.52	0.51	0.800	0.785	1.7
Siliceous minette.....	13.5	12.2	7.4	6.7	10.5	9.5	0.9	0.8	33	31	0.2	0.2	0.08	0.07	0.720	0.652	9.3
Calcareous minette.....	7.4	6.8	6.3	5.8	16.6	15.2	1	0.9	30.6	28	0.2	0.2	0.08	0.07	0.700	0.640	8.3
Manganese ore.....	7.5	6.9	2.2	2	0.6	0.5	0.3	0.3	1.3	1.2	52.6	48.5			0.195	0.180	7
Open-hearth slag.....	21.7	21.5	4.7	4.7	36.1	36	7.2	7.2	13.2	13	8.2	8.1			0.600	0.600	
Cinder (from reheating fur- naces).....	23.1	23	3	3	0.2	0.2	0.3	0.3	55.1	55	0.5	0.5			0.035	0.035	
Sinter.....	10.5	10	7.4	7	6.5	6.2	0.9	0.8	51.25	48.6	0.4	0.4	0.04	0.04	0.540	0.510	5
Miscellaneous scraps.....									78								
Fine iron from converter spittings.....	8.3	8.3	6.8	6.8	31.8	31.8	1.3	1.3	28.42	28.4	3.9	3.9	0.01	0.01	3.84	3.84	
Coke ash.....	47.6		32.3		2.4		1.15		7		0.2		0.14		0.35		
Per Cent																	
Coke: moisture, 2.45 per cent; ash, 13.32 per cent. Composition of top gases: CO <sub>2</sub> 9.2																	
CO 27.6																	
CH <sub>4</sub> 0.2																	
H <sub>2</sub> 1.5																	
N <sub>2</sub> 61.5																	
100.00																	



TABLE 5.—(Continued)  
ANALYSES, APRIL, 1934, PER CENT

	SiO <sub>2</sub>		Al <sub>2</sub> O <sub>3</sub>		CaO		MgO		Fe		Mn		S		P		Mois- ture
	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	
Normandy siliceous ore.....	14.2	14	7.9	7.8	3.9	3.8	2.16	2.1	48	47.4	0.34	0.33	0.24	0.24	0.925	0.915	1.22
Siliceous minette.....	13.4	12.1	5.5	5	10.9	9.9	1.4	1.3	34.9	31.6	0.22	0.2	0.06	0.05	0.750	0.680	9.26
Calcareous minette A.....	6.2	5.6	4.7	4.2	17.1	15.4	1.4	1.3	33.3	30.2	0.24	0.22	0.06	0.05	0.675	0.610	9.34
Calcareous minette B.....	6.05	5.5	5.74	5.2	14.9	13.4	1.6	1.4	35.5	32.1	0.28	0.25	0.12	0.11	0.675	0.610	9.51
Manganese ore.....	10.9	10.6	7.57	7.4	1	1	0.2	0.2	16.74	16.3	34.05	33			0.330	0.320	2.8
Sinter (pyrites cinder and flue dust).....	8	7.7	5.31	5.1	7.6	7.3	1.22	1.2	56.5	54.5	0.4	0.4	0.18	0.17	0.500	0.485	3
Open-hearth slag.....	19.6	19.5	4.2	4.2	40.7	40.5	7.23	7.2	11.13	11	7.95	7.9			1.4	1.4	0.5
Reheating-furnace cinder.....	24.9	24.9	3.06	3	2.1	2.1	0.7	0.7	52.52	52.5	0.43	0.4			0.185	0.185	
Rolling-mill cinder.....	1.2	1.1	1.91	1.8	1.5	1.4	0.36	0.38	69.6	64.4	0.55	0.5			0.075	0.070	6.8
Miscellaneous scraps.....								78	78								
Iron extracted from conver- ter spittings.....			7.5	7.5	43	43	0.4	0.4	0.7	0.7					3	3	
Lime phosphate.....	11	11											0.02	0.02	13	13	
Coke ash.....	48.7		34.6		1.8		0.8		6.5		0.10		0.16		0.380		

Per Cent

Coke: moisture, 2 per cent; ash, 11.35 per cent.

Composition of gas: CO<sub>2</sub> 13.25O<sub>2</sub> 0.31

CO 26.11

TABLE 5.—(Continued)  
ANALYSES, JANUARY, 1936, PER CENT

	SiO <sub>2</sub>		Al <sub>2</sub> O <sub>3</sub>		CaO		MgO		Fe		Mn		S		P		Mois- ture
	Dry	Raw	Dry	Raw	Dry	Raw	Dry	Raw	Dry	Raw	Dry	Raw	Dry	Raw	Dry	Raw	
Normandy siliceous ore.....	15.2	14.7	8.37	8.1	3.25	3.1	1.72	1.7	47.85	46.4	0.41	0.4	0.19	0.18	0.775	0.750	3.1
Calcareous minette A.....	6.5	6	4.22	3.8	17.8	16.3	1.36	1.2	32	29.3	0.27	0.25	0.05	0.05	0.750	0.680	8.48
Calcareous minette B.....	6.2	5.6	4.87	4.4	14.8	13.4	1.4	1.3	35.88	32.7	0.30	0.27	0.07	0.06	0.710	0.650	8.9
Manganese ore.....	5.7	5.4	5.5	5.2	0.1	0.1			9	8.5	46.4	43.6			0.148	0.140	5.5
Sinter (pyrites cinder and flue dust).....	6.5	6	4.83	4.5	4.1	3.8	0.68	0.6	58.3	54	0.3	0.3	0.18	0.16	0.375	0.340	8
Open-hearth slag.....	21.9	21.5	4.84	4.8	35.8	35.5	6.19	6	12.4	12	10.1	10			0.502	0.480	
Reheating-furnace cinder....	9.3	9.3	6.07	6	0.4	0.4	0.21	0.2	62.8	62.	0.53	0.5			0.050	0.050	
Rolling-mill cinder.....	3	3	1.91	1.9	0.7	0.7	0.22	0.2	71	70	0.37	0.35			0.035	0.032	2
Miscellaneous scraps.....									78								
Iron extracted from conver- ter spittings.....									80								3
Lime phosphate.....	11	11	7.5	7.5	43	43	0.4	0.4	0.7	0.7			0.02	0.02	13	13	
Limestone.....	2	1.6			54.5	45	0.28	0.23	0.42	0.35					0.052	0.043	17
Coke ash.....	48.7		34.6		1.8		0.8		6.5		0.10		0.16		0.380		

Per Cent

Coke: moisture, 3.75 per cent; ash, 11.30 per cent. Composition of gas: CO<sub>2</sub> 12.38O<sub>2</sub> 0.25

CO 25.4

H<sub>2</sub> 2.25CH<sub>4</sub> 0.4N<sub>2</sub> 59.32

100.00

TABLE 6.—Average Burden Hematite Pig Iron, April, 1936, No. 4 Furnace<sup>a</sup>

	254.3 <sup>b</sup>	Production in 24 hr. (monthly average), tons
Spanish ores.....	197.1	270.9
Swedish ore.....	229	20.9
Algerian ore.....	21.2	854.2
Morocco Rif ore.....	35.7	50.5
Manganese ore.....	535.9	2,690 (95,000 cu. ft.)
Sinter from pyrite cinder.....	213.2	30,400
Reheating furnace cinder.....	202.5	18,200
Scrap iron.....	291.2	665
Limestone.....		200
Total.....	1980	

Volume of blast as given by daily reports:

Per metric ton of iron, cu. m.....

Per hour, cu. m.....

Per minute, cu. ft.....

Heat of blast, deg. C.....

Temperature at top, deg. C.....

## ANALYSES, APRIL, 1936, PER CENT

Material	SiO <sub>2</sub>		Al <sub>2</sub> O <sub>3</sub>		CaO		MgO		Fe		Mn		S		P		Moisture	Composition			
	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet		Fines	Mid-dlings	Lumps	
Spanish ore oxide.....	7.5	6.8	3.4	3.1	1.1	1	0.55	0.5	54	43.6	0.8	0.7	0.77	0.70	0.028	0.025	10.25	55	35	10	
Spanish ore calcined carbonate.....	6.8	6.7	2.15	2.1	2.85	2.8	4	3.9	56.4	55.25	0.92	0.9	0.306	0.300	0.010	0.010	2.2	60	30	10	
Swedish ore.....	6.9	6.9	3.7	3.7	4.8	4.8	3.5	3.5	48.8	48.7	4.75	4.74			0.025	0.025	0.2	28	57	15	
Algerian ore.....	1.48	1.4	2.2	2.1	3.06	2.9	1.4	1.3	55.8	52.6	2.2	2.1			0.025	0.024	5.8	35	35	30	
Morocco Rif ore.....	3.05	3	1.43	1.4	1.53	1.5	0.3	0.3	63.5	62.7			0.153	0.150	0.025	0.025	1.5	10	15	75	
Manganese ore.....	5.7	5.4	5.5	5.2	0.1	0.8	0.7	0.61	0.6	80.87	57.5	9	8.5	46.5	43.7	0.148	0.140	5.5	5	75	20
Sinter from pyrite cinder.....	6.35	6	4.81	4.5	0.8	0.7	0.32	0.3	62.56	62	0.4	0.4	0.14	0.13	0.018	0.017	5	20	80		
Reheating-furnace cinder.....	11	11	4.7	4.7	1.1	1.1	0.32	0.3	62.56	62					0.057	0.055		5	45	50	
Scrap iron.....									95												
Limestone.....	0.3	0.3			49.8	49.8	5.22	5.2	0.5	0.5	0.10		0.04		0.010	0.010		5	95		
Coke ash.....	48.3		36.5		1.8		0.8		5.6						0.360						

Coke: moisture, 2.1 per cent; ash, 11.3 per cent. Composition of gas: CO<sub>2</sub> Per Cent 9.71 CO 29.80 H<sub>2</sub> 2.1  
O<sub>2</sub> 0.15 CH<sub>4</sub> 0.4 N<sub>2</sub> 57.84

100.00

<sup>a</sup> No. 4 furnace could easily produce 450 tons of pig iron. <sup>b</sup> All quantities in this column in kilograms.

gastight seal is on the junction of these two parts. The stacks of our furnaces have grown vertically and our No. 3, having made about 700,000 tons of pig iron, has grown between 5 and 6 ft. vertically. From

TABLE 7.—*Analysis and Sieve Tests of Flue Dust*

	Analysis, Per Cent		
	Thomas Pig Iron		Hematite Pig Iron
	Rapid Driving	Slow Driving	
Ignition loss.....	14.88	16.75	21.7
SiO <sub>2</sub> .....	9.70	9.80	7.2
Al <sub>2</sub> O <sub>3</sub> .....	6.47	7.13	2.8
CaO.....	10.40	12.60	3.45
MgO.....	1.69	2.23	1.71
FeO.....	16.00	20.18	29.4
Fe <sub>2</sub> O <sub>3</sub> .....	37.11	28.60	25.5
MnO.....	0.73	0.58	1.2
P <sub>2</sub> O <sub>5</sub> .....	1.694	1.54	0.12
Total.....	98.674	99.41	93.08
Insoluble.....	11.50	11.10	9.81
Fe.....	38.43	35.72	40.74
Mn.....	0.53	0.42	0.87
S.....	0.09	0.18	0.38
P.....	0.74	0.675	0.053

	Sieve Tests, Per Cent		
	Thomas Pig Iron		Hematite Pig Iron
	450 Tons per 24 Hr.	250 Tons per 24 Hr.	200 Tons per 24 Hr.
Mesh per sq. cm.			
On 324.....	9.2	0.8	4.6
On 900.....	44.5	10.6	12.1
On 4900.....	39.7	81	76
Through 4900.....	6.6	7.6	7.3
Total.....	100.0	100.0	100.0
Density.....	1.295	1.275	1.131

time to time we take off a few rows of bricks to bring point *B* in Fig. 19 to the place of point *A*. We believe that these difficulties are due to zinc fumes, which cause the joints and bricks to swell. We did not have this trouble when smelting iron ores without pyrite cinder.

We have never made use of auxiliary tuyeres and have none in two furnaces.

No. 1 furnace is being rebuilt at the present time (Fig. 15), after a campaign of over one million tons of pig iron on a yield of about 30 per cent as an average, and a consumption of over 4,500,000 tons of raw materials.

We have also contemplated the preparation of the ore burden—that is, crushing and screening and sintering of the fines—but the benefit expected from that improvement in 1931 is of course much less now with lower figures of coke consumption and lower coke prices. With the



FIG. 14.—BLAST FURNACES AT DENAIN.

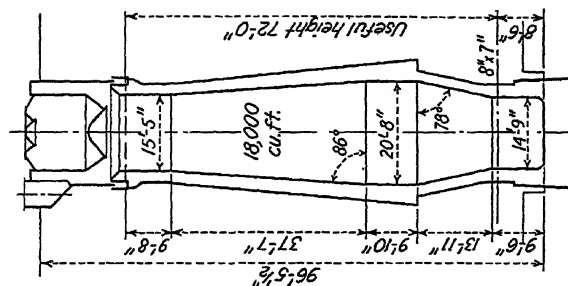
present experiments of our government, things may change greatly and other conclusions may have to be derived.

The raw material varies considerably, from what may be termed fine ore (sinter, largely of Spanish and Algerian ores) to large lumps, the average size of which may be estimated at 15 or 20 inches.

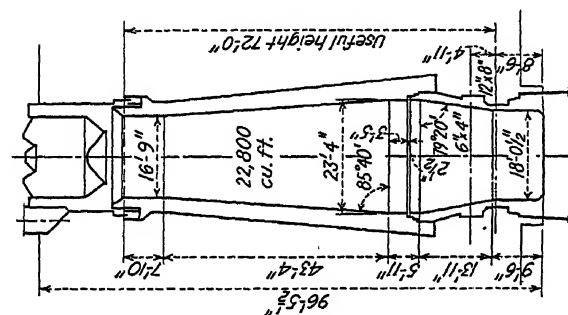
Coke is of average quality, ash ranging from 11 to 11.5 per cent, moisture from 2 to 3 per cent and size from 6 to 7 inches.

The average Thomas iron analysis is as follows: Si, 0.35 per cent; Mn, 1.10; P, 1.80; S, 0.04.

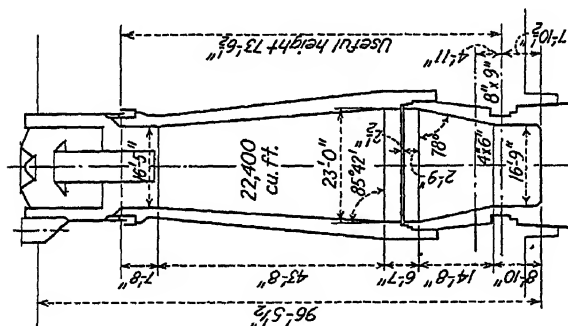
The iron goes into a mixer of 650 tons capacity,  $1\frac{1}{2}$  miles from the furnaces. Much of the sulphur leaves the iron and forms a slag crust on top of the ladle. The average sulphur content of the iron leaving the mixer is 0.025 per cent. The temperature of the iron should be  $1225^{\circ}$  to  $1230^{\circ}$  C. when blown in the converter;  $1190^{\circ}$  is the lower limit for good blowing and any temperature below that leads to heavy losses through spittings. This mixer, containing 550 tons of iron, was not emptied during the last strike, because the plant was in the hands of the workmen



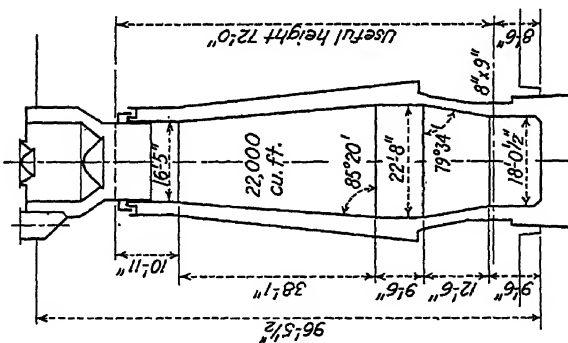
HF 4  
1931  
Fig. 18.



HF 3  
1930  
Fig. 17.



HF 2  
1929  
Fig. 16.



HF 1  
1935  
Fig. 15.

FIGS. 15-18.—LINES OF BLAST FURNACES AT DENAIN.

and hundreds of them prevented us from tilting the mixer. The heating is done ordinarily with blast-furnace gas by two regenerators for heating the air combustion. We resumed work after 15 days and heated the mixer with blast-furnace and coke-oven gas, having installed a fan to give the necessary air, and were able to remelt the iron in a rather short time.

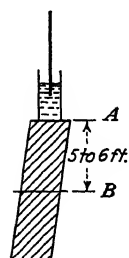


FIG. 19.—  
VERTICAL  
GROWTH OF  
STACKS RE-  
DUCED BY  
REMOVING  
BRICKS BE-  
TWEEN A  
AND B.

### FLUE DUST

Returning to burdening the furnaces, I should like to call attention to the great difference in physical properties of the flue dust produced by slow and rapid blowing (Table 7). The former leads to much difficulty in the sintering plant and great care must be taken to have an adequate bedding material and adjust the right moisture for best results.

Table 8 shows the distribution of the iron losses in slow and rapid driving. In both, the dust escaping the scrubber towers is very lean and leaves the disintegrators with the washing water, where there are no reclaiming basins. Thus from 3.3 to 3.5 per cent of the iron charged is lost.

TABLE 8.—*Iron Loss in Flue Dust, in Relation to Total Iron Charged*

	Rapid Driving, February, 1930	Slow Driving, April, 1934	Present Operation, January, 1936
Iron charged per ton pig iron, kg. ....	1,111.1	1,025.7	1,044.9
Iron in ladle scraps and other scraps, kg. ....	3	0.3	0.2
Remainder. ....	1,108.1	1,025.4	1,044.7
Iron in pig, kg. ....	950	950	950
Iron in collected heavy dust, kg. ....	111	35.7	69
Iron in slag, kg. ....	8	8	8
Total. ....	1,069	933.7	1,027
Iron loss (difference) weight, kg. ....	39.1	31.7	17.7
Iron loss (difference) weight, per cent. ....	3.5	3.3	1.7

These results show the vast difference between the minette ores, with their tendency to explode in the furnace, and other ores as used in our No. 4 furnace for varying pig-iron grades. With a raw material that may be called fines (Spanish roasted carbonates and Algerian ores, amounting to 485 kg. in the burden) the amount of flue dust produced is 20 kg. per ton of pig iron, with rather slow blowing. But, with a production of 450 to 500 tons in 24 hr., the amount would not exceed 80 kg. per ton of iron.

## CONCLUSION

Thus we may conclude that the minette ores are quite suitable to produce basic pig iron, with low silicon for the conversion into steel by the basic Bessemer process. Practice should be improved with a more

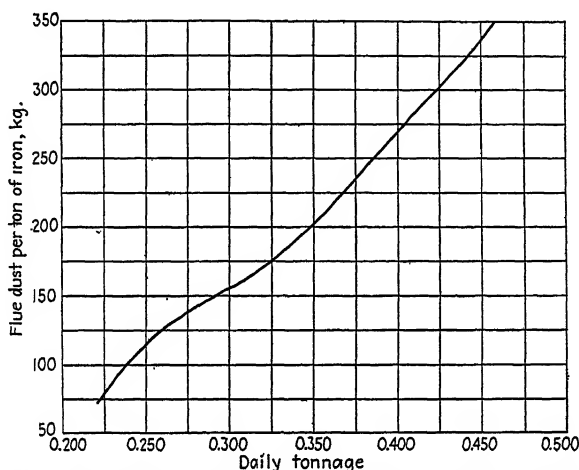


FIG. 20.—RELATION BETWEEN PRODUCTION OF FLUE DUST AND DAILY TONNAGE AT DENAIN.

physically regular burden, especially when faster driving has to be applied. At our plants, this would be much easier, because we charge less than two tons of minette ore per ton of iron. The way has been shown by the Larre Works and we are awaiting the right time to go ahead on this improvement.



## Recovery of Blast-furnace Flue Dust from Scrubber Water

BY T. B. COUNSELMAN,\* MEMBER A.I.M.E.

(Cleveland Meeting, October, 1936)

AN iron blast furnace of 1000 tons daily capacity will produce about 100,000 cu. ft. per minute of blast-furnace gas. This contains about 25 per cent of carbon monoxide, and has a B.t.u. value of about 95. This gas is used primarily for heating the stoves of the blast furnace, and secondarily, under boilers, for steam production. Occasionally it is also used in gas engines.

The raw gas coming out of the furnace carries about 10 grains of flue dust per cubic foot of gas, under best operating conditions. With the furnace "rolling" or slipping, this quantity may temporarily be greatly increased. This dust would, of course, deposit on the checkers of the stoves, or plug the burners under the boilers; therefore the gas must be cleaned.

### FLOW SHEET

The first step in the cleaning operation, as shown by the flow sheet, Fig. 1, is a dry dust catcher, of which there are several forms. The partially cleaned gas next goes to a primary wet washer, where water sprays knock down most of the solid particles. If further cleaning is desired, the gas may then go to electrical precipitation. Again, the dust removed is collected in water. Dry dust catchers reduce the dust content from 10 grains to between 4 and 6 grains per cubic foot, and recover roughly half of the total flue dust in the gas. The wet washers recover most of the remaining dust, reducing the dust content to about  $\frac{1}{4}$  grain per cubic foot. Electrical precipitators, if used, further reduce the dust content to about 0.01 grain per cubic foot of gas. The flow sheet shows the dust content of the gas at various steps in the treatment and also the content of solids in the water. It should be noted that some plants use less water on the primary wet washer than indicated, and that often the solids content of the scrubber water will be 300 grains per gallon, or even much higher.

*Reasons for Recovering Flue Dust.*—There are two main incentives for recovering flue dust from the scrubber water: (1) the value of the dust; (2) stream or lake pollution, where such a reason applies.

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Essentially this dust is iron ore, worth \$4.50 per ton base price at lower lake ports. The recovered wet dust from a 1000-ton furnace would amount to about 40 tons a day. Assigning a nominal value of only two dollars per ton would mean a saving of nearly thirty thousand dollars a year and would give the furnace fourteen thousand tons of very cheap ore.

Federal and state authorities are becoming more and more insistent on plants keeping this flue dust out of the navigable rivers and harbors, so as to avoid periodic dredging. In fact, contamination of all streams and lakes is being prohibited more and more universally. Even small blast-furnace plants, which make only a small amount of wet dust,

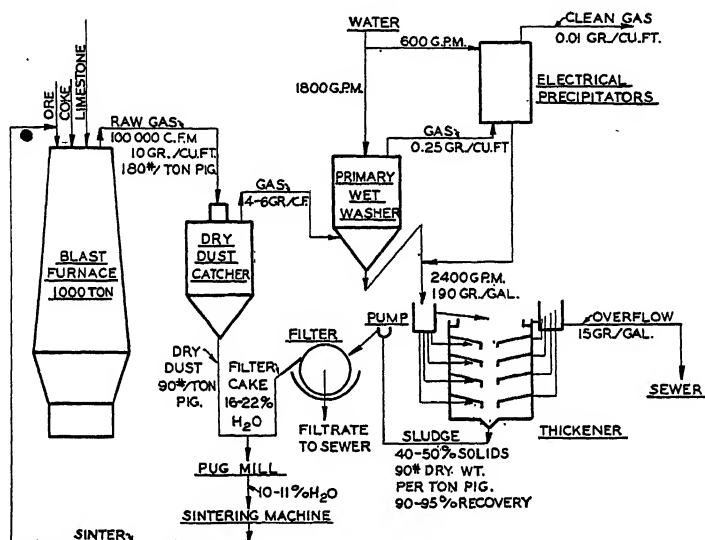


FIG. 1.—FLOW SHEET OF CLEANING BLAST-FURNACE GAS AND RECOVERING FLUE DUST.

insufficient to justify recovery economically, are taking steps to avoid further pollution and future trouble with the authorities.

*Clarity Desired.*—Looked at from the economic viewpoint, most plants aim at a recovery of 90 per cent of the suspended solids in the scrubber water. Neglecting consideration of electrical precipitation for the moment, with scrubber water containing 150 grains per gallon, this means a clarified effluent to the stream carrying 15 grains per gallon. Naturally, with scrubber water originally containing, say, 300 grains, a 90 per cent recovery is not sufficient, and the plant will still want a 15-grain overflow, or about 95 per cent recovery.

From the standpoint of stream pollution, still better clarities are desirable. Even rather dirty lake or river water will have a turbidity of say 200 p.p.m., or 12 grains per gallon. It has become customary practice, therefore, where no electrical precipitators are used, to require

an effluent carrying 10 to 12 grains. Incidentally, some operators ask for overflows of 5 grains. This is not economically feasible. The curve of area requirements flattens off very rapidly below about 8 grains, and a 5-grain overflow would require about three times as much thickener capacity as a 10-grain overflow.

The use of electrical precipitators changes the picture considerably. The solid particles recovered in these precipitators consist practically of a fume. The particles are so finely divided that it would be an optimistic guess to assume that 50 per cent of the weight would settle and be recovered.

Taking as typical the figures given on Fig. 1, in 100,000 cu. ft. per min. of gas, reducing the dust content of this gas from 0.25 to 0.01 grains per cubic foot would mean knocking down 5000 lb. of solids per day. Assuming that 50 per cent of this, or 2500 lb., would report in the overflow anyway, and taking the total volume of water at 2400 gal. per min. as shown on the flow sheet (20 gal. per 1000 cu. ft. per min. for wet scrubbers, and 4 gal. per 1000 cu. ft. per min. for electrical precipitators) the quantity of suspended solids in the clarified overflow will be increased by 5 grains from this source alone. Therefore, clarification equipment that would give a 10-grain overflow on wet washer dust will automatically give a 15-grain overflow if electrical precipitators are used (for all of the gas). This gets back to a 90 per cent recovery on a 150-grain scrubber water, and seems to be the optimum clarity to consider.

*Thickening.*—In clarifying the overflow, the solids are naturally consolidated to a thickened sludge. This may be thickened easily to 60 or 63 per cent solids, and still be pumpable. The degree to which this sludge should be thickened is determined entirely by the next step in the treatment, and by local conditions. The most usual treatment of this sludge is filtration, to prepare it for sintering. In that case, it should be thickened only to about 40 per cent solids. This gives the most uniform cake thickness on the filter, and, consequently, the dryest cake.

#### METHODS OF CLARIFYING

Probably the oldest method of clarifying scrubber water was simply to impound it in some sort of a basin. When the basin had become pretty well filled with solids, the flow was switched to another basin, and the drained but very soupy solids in the first basin were excavated, possibly with a clam shell. It was probably a somewhat messy job. This is discussed in the past tense because, so far as known, with one interesting exception, plain settling basins are no longer used.

At the Gary plant of the Carnegie-Illinois Steel Co., long rectangular concrete basins already built are used for clarifying scrubber water. Settled sludge is removed continuously from these, however, by means of suction pumps, which travel at a uniform rate, back and forth across,

and from end to end of the basins. The recovered sludge is not thick enough to filter, and therefore is pumped to a traction type of thickener for resettling, the very dirty thickener overflow being returned to the larger settling basins. This ingenious installation, which was practicable only because of existing local conditions, is really a cross between the old plain settling basins and the continuously, mechanically cleaned thickeners of today.

The most widely used clarification device for the recovery of flue dust from scrubber water is the round thickener, with slowly revolving plow arms, which continuously rake the settled solids to a central discharge point. There are now some 55 installations of this type of thickener in this country and abroad, serving 120 blast furnaces. The first installation was made in 1916 and the type of unit has undergone a gradual evolution.

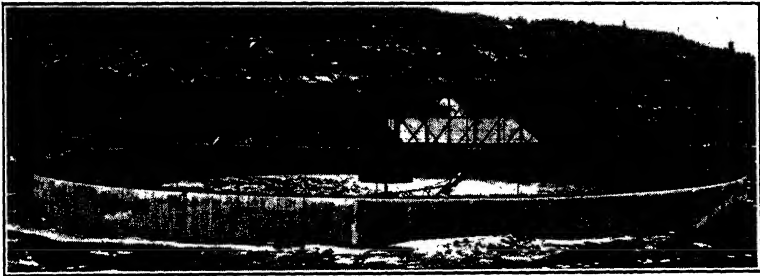


FIG. 2.—EARLY TYPE OF THICKENER.

The earliest was the center-shaft center-drive thickener, adopted from the metallurgical industry (Fig. 2). These units were of relatively small capacity, serving one or two furnaces. A steel truss bridge carried the weight of the vertical center shaft and raking mechanism, and the drive unit. This type of thickener is now obsolete, although many are still in service.

As larger capacity was required for larger blast-furnace plants, the traction thickener (Fig. 3) was developed (again adopted from the metallurgical industry). In this unit, the raking blades are carried on a more or less submerged truss, one end of which is supported on a central concrete or steel pier, the other end on the peripheral ring wall. Sometimes this outer support is on a curved railroad rail, with a steel driving wheel, sometimes on the concrete wall itself with a rubber-tired driving wheel. This last modification has not been overly successful, the rubber tire being too difficult to hold on the cast-iron heart or core. A number of these traction thickeners have been installed, the largest installation consisting of two units, each 160 ft. in diameter, at the South Works of the Carnegie-Illinois Steel Co. at South Chicago. These two units serve eleven large blast furnaces, and are rated to handle 35 million gallons of scrubber water a day. The traction thickener shown in Fig. 3, at the

plant of the Inland Steel Co., Indiana Harbor, Ind., is 140 ft. in diameter, serves four large blast furnaces and is rated to handle 14 million gallons a day, or 10,000 gal. per minute.

The next condition to be met was lack of space at existing older plants for thickeners requiring such large areas. Tray thickeners had been used at metallurgical plants, and a few installations were made of the early so-called open type of tray thickener. A good example is the installation of a 60-ft. two-compartment machine at the Mark plant of the Youngstown Sheet and Tube Co., Indiana Harbor. In this type of tray thickener, all of the feed entered the top compartment at the center, all of the sludge was withdrawn from the lower compartment, but

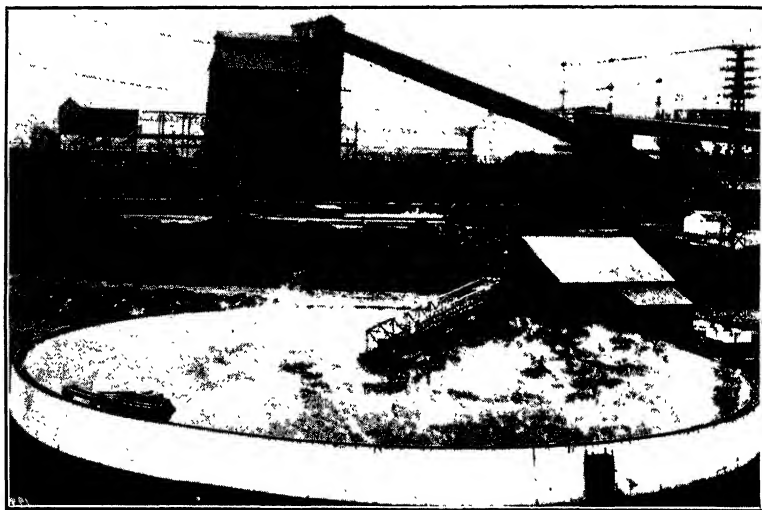


FIG. 3.—TRACTION TYPE OF THICKENER, INLAND STEEL COMPANY.

clarified overflows were taken from each compartment. The mechanism was still carried from a bridge truss, the raking arms being driven from a vertical center shaft.

This arrangement, though an improvement, still was not entirely satisfactory, the total area being somewhat inefficiently used and too much area being required. The filter-thickener, adopted from the sugar-beet industry, was tried out for flue dust. In this machine, so-called "socks" are suspended in a rather deep single-compartment tank. Vacuum is applied to the inside of the socks for a definite time cycle, the clarified effluent being drawn through the socks, and of course, a filter cake building up on the outside. At definite intervals, the vacuum is cut off, a back-pressure created, and the socks shaken mechanically to dislodge the cake, which settles to the bottom of the tank. Revolving plow arms rake the solids to the center, as in the earliest type of thickener.

This machine showed some promise, but it was very complicated mechanically and did not stand up under the grueling, continuous service of a blast-furnace plant. The socks became blinded by lime in the scrubber water; holes developed frequently, ruining the clarity of the effluent; maintenance of socks alone proved excessive; the timing and shaking mechanism was too intricate and delicate for ordinary plant labor to handle. Therefore after two or three installations of commercial size had been thoroughly tried out, this thickener was abandoned.

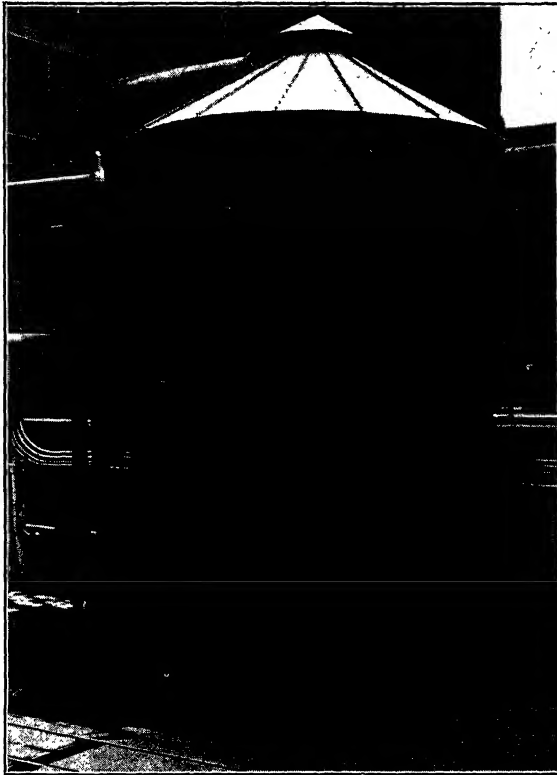


FIG. 4.—BALANCED TRAY THICKENER, FORD MOTOR COMPANY.

Meanwhile, an improved tray thickener, called the balanced type, had been developed. In this machine, the original feed was divided mechanically and entered each tray or compartment individually. A clarified effluent was obtained from each compartment. The sludge settled out was raked to the center of each compartment and discharged into a boot, which delivered it below the sludge level in the next lower compartment. In this way the sludge was prevented from dispersing and having to be re-settled, as had been necessary in the earlier open tray thickeners. The mechanical features were improved in many respects, one of the most

important being the hanging of the entire mechanism from a worm gear carried on a continuous ring of  $1\frac{1}{8}$ -in. balls forming a ball bearing 6 ft. in diameter. This reduced the power, eliminated the necessity for a bridge superstructure, and because of the diameter of the large ball bearing carrying the weight, eliminated any side sway of the mechanism. This permitted the use of a larger number of compartments, which, coupled with the increase in capacity per compartment, made it possible to handle the scrubber water from a single blast furnace in a space approximately the diameter of a stove. Such space is ordinarily available, even in a cramped plant. The latest installation of this type is

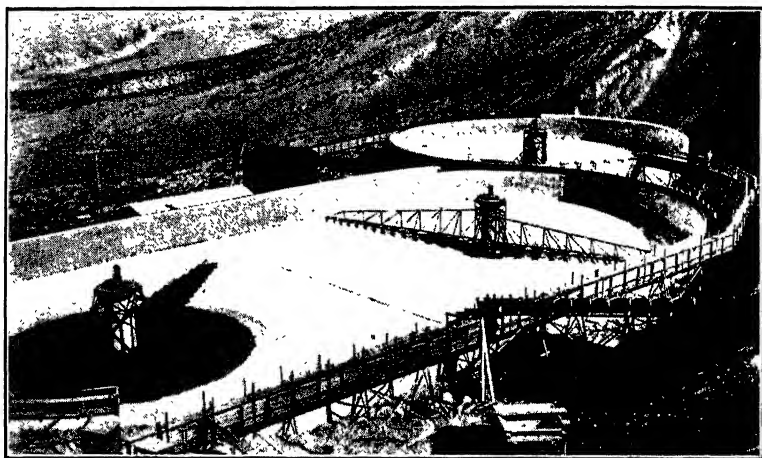


FIG. 5.—TORQ THICKENER, GRAND COULEE DAM.

illustrated in Fig. 4. This shows one of the two thickeners installed nearly a year ago in the Rouge plant of the Ford Motor Co. at Dearborn. Each of these six-compartment balanced tray thickeners, 22 ft. 6 in. dia. by 26 ft. 0 in. deep, serves a 750-ton blast furnace; it is designed to handle 1800 gal. per min. of scrubber water, but has handled over 2000 gal. per min. Performance data are given in Table 2.

Meanwhile, a still greater improvement has been made in the mechanism for large-diameter single-compartment flue-dust thickeners. This is the Torq thickener, originally developed for service in desilting Colorado River water for irrigation purposes. This mechanism is carried on a central pier, the weight being carried on a large-diameter ball bearing, as in the balanced tray thickener. The Torq thickener is driven from the center, by means of an internal ring gear, and practically all of the mechanism is submerged. The Torq feature consists of hinging the arms in such a way that in case of an overload, or starting up a machine when the raking blades are partly buried in sludge, the arms swing backward and upward, riding over the settled solids but still carrying a full raking

load. All this takes place without increasing the torque on the motor, and without any attention on the part of the operator. In fact, the arms being entirely submerged, the operator ordinarily would not be aware of what was happening.

Two machines of this type, 70 ft. in diameter, have recently been installed by the Republic Steel Corporation at the Corrigan-McKinney plant in Cleveland, and should be in operation by the time this paper is presented. Operating data, of course, are not yet available. This type of thickener is illustrated in Fig. 5, which shows machines installed at Grand Coulee dam, where they are used for clarifying water for re-use in the sand-grading plant. Also, two machines are shown installed in a single basin. This is feasible, with this type of thickener.

Table 1 shows operating data on a traction thickener; Table 2, data on a balanced tray thickener.

TABLE 1.—*Data on Traction Thickener*

Size.....	140 ft. dia. by 17 ft. center depth
Number of blast furnaces served.....	4
Rated capacity.....	10,000 gal. per min.
Corresponding overflow clarity, grains per gal. <sup>a</sup> ...	10
Performance data, 24-hr. sampling for 7-day period:	
Number of blast furnaces operating.....	3
Furnace capacity, pig iron, tons.....	2150
Gas production, cu. ft. per min.....	200,000
Total scrubber water to thickener, gal. per min.....	5880
Dust content of feed to thickener, gr. per gal.	108.7
Dust content of thickener overflow (ranged from 6.2 to 10.2 gr. per gal.), gr. per gal. ....	8.3
Recovery of dust in thickener, per cent. ....	92.5
Dry-basis screen analysis of wet dust:	
	MESH
	+40
	+60
	+80
	+100
	+200
	-200
	PER CENT
	0.33
	1.28
	3.15
	4.04
	15.68
	84.32

<sup>a</sup> No electrical precipitators used.

#### WITHDRAWING AND DRYING SLUDGE

Customarily the sludge is withdrawn from the thickener by means of diaphragm pumps. These are provided with an adjustable length of stroke, and are really metering devices for withdrawing a definite volume of sludge. In this way, a thick sludge can be obtained, because, the rate of withdrawal being under close control, the possibility of the sludge coning and the pump sucking through too much water is avoided. Piping usually is arranged so that the sludge withdrawn from the thickener can be returned to the feed, if desired. There are several reasons for this



arrangement. Frequently the filter and sintering plant operate only one or two turns, while scrubber water must be clarified 24 hr. a day. By recirculating the underflow, the thickener can be made to provide the necessary storage for this condition. Also, if for any reason the sludge is too thin to be filtered advantageously, the sludge can be recirculated until its consistency has been built up to the proper point.

TABLE 2.—*Data on Balanced Tray Thickener<sup>a</sup>*

Size.....	22 ft. 6 in. dia. by 26 ft. 0 in. deep
Number of compartments.....	6
Number of blast furnaces served.....	1
Rated capacity of thickener, gal. per min.....	1800
Corresponding overflow clarity, gr. per gal. <sup>b</sup> .....	15
Performance data, thickener serving furnace making basic iron:	
Furnace capacity, pig iron, tons.....	750
Gas production, cu. ft. per min.....	50,000
Total flue-dust production per ton of pig iron, lb.....	120
Dust content of gas from dry catcher, gr. per cu. ft.....	5
Dust content of gas from primary wet washer, gr. per cu. ft.....	0.4
Dust content of gas from electrical precipi- tators, gr. per cu. ft.....	0.04
Water used on wet washers, gal. per min....	1250
Water used on electrical precipitators, gal. per min.....	400
Total water to thickener, gal. per min. <sup>c</sup> ....	1650
Temperature of water to thickener, deg. F..	130
Temperature of thickener overflow, deg. F..	110
Dust content of feed to thickener (5 months average), gr. per gal.....	78
Dust content of thickener overflow (5 months average) gr. per gal. <sup>d</sup> .....	7.4
Recovery of dust in thickener, per cent.....	90.5
Dry-basis screen analysis of wet flue dust:	
	MESH
	PER CENT
	+100
	13.6
	+200
	34.1
	+240
	43.5
	-240
	56.5

<sup>a</sup> A5TB.

<sup>b</sup> Electrical precipitators used.

<sup>c</sup> Duplicate thickener handling 2050 gal. per minute.

<sup>d</sup> Electrical precipitators not operating. When these were operating overflow clarity averaged about 14 gr. per gallon.

There are several ways of handling the thickened flue-dust sludge. If the quantity is not large, it may be run to a pit, allowed to drain and later loaded out by a locomotive crane and sent to the ore yard. A somewhat better way, sometimes practiced, is to pump the thickened sludge directly into a dry-dust car, letting the water filter out through the dry

dust. In either case, the sludge eventually reaches the ore yard in a rather sloppy condition, where it may be mixed with ore by turning it over with the bridge crane. Another method of handling is to pump the thick sludge to shallow impounding areas, filling one, draining, and letting the flue dust dry by solar evaporation. This method requires rather large areas for any quantity of dust, and a rehandling that is not particularly cheap.

The best practice is to filter the thickener sludge by continuous vacuum filtration. Either a drum or disk filter is generally used. Some other kinds have been tried, but have not found wide application. Each type of filter has certain advantages. For example, flue-dust filter cake cracks badly, and for very fine flue dust, in order to get a cake moisture that is sinterable, flappers or vibrating pressure rolls have to be used. These compress the cake and close the cracks, resulting in 2 or 3 per cent lower cake moisture. Flappers or rolls can be used only on drum filters. On the other hand, with disk filters greater filter area can be obtained in limited floor space, and no time need be lost in changing filter cloths. The capacity of each type is the same, per square foot of filter surface. This will vary with the screen analysis and physical characteristics of the flue dust, but a fair range is 800 to 1200 lb. dry basis per square foot per day. Cake moisture will also vary widely with the physical characteristics of the flue dust, and will range from 16 to 26 per cent. These moistures are in general too high for sintering direct, therefore the filter cake usually is mixed with dry flue dust in a pug mill, to give a resultant moisture of about 10 to 11 per cent. This is not always done; in certain instances coating the outside of the lumps of filter cake with dry dust, so as to preserve the porosity of the bed, makes it possible to sinter cake with surprisingly high moisture. A notable example is the Gary plant of Carnegie-Illinois Steel Company.

#### HANDLING FILTER CAKE

The filter cake is handled in various ways. Sometimes the cake, together with dry flue dust, is charged back into the blast furnace without agglomeration of any kind. Generally, however, the mixture of wet and dry dust is agglomerated. Nodulizing, similar to that in cement-mill practice, has been tried. The Youngstown Sheet and Tube Co. had two nodulizing kilns at Mayville, Wis., but this plant has been closed. The objection to nodulizing was the glazing of the surface, which made penetration of the gases in the blast furnace too slow. If glazing were avoided by temperature control, the interior of the nodule was not agglomerated, and the production of flue dust was increased.

One of the most attractive methods of agglomerating, from a theoretical standpoint, is briquetting. The use of a brick press alone is not suitable, since the particles are not really agglomerated, even with a

binder, except by heat. The Grondal system of briquetting was thoroughly tried out at Moose Mountain, Canada, and while it produced a very desirable furnace product, was never mechanically successful.

The usual method of agglomeration is sintering. Two systems are in use: (1) the Dwight-Lloyd machine, consisting of a continuous strand of pallets sliding over a wind box; (2) the Greenawalt system, consisting of a single large pan operated in batch fashion. In both processes the coke breeze in the dry dust furnishes short-flame fuel, scattered uniformly through the bed. Air is drawn down through the bed by an exhaust fan creating a vacuum of about 18 in. of water. The top surface is ignited by a very intense flame, oil or gas, under a reverberatory hood, the temperature reaching 2500° F. The carbon in the bed is ignited, and because the air is drawn down through the bed successive carbon particles are ignited, the heat traveling gradually downward to the grates. This raises the flue-dust particles to a temperature of incipient fusion, so that when discharged and cooled the sinter looks somewhat like coke. When this sinter is charged back into the blast furnace, it no longer has a chance to escape as flue dust. Because of the porosity of the sinter, the surface exposed is large, offering ready access to the reducing gases. Sinter, in general, speeds up a blast furnace and increases its capacity.

## DISCUSSION

*(William A. Haven presiding)*

W. A. HAVEN,\* Cleveland, Ohio.—Two very large installations were described here. One was at Inland and the other one at Corrigan-McKinney, on which Mr. Counselman said he has not had an opportunity to get data. The fact of the matter is that the installation is just going into operation today. The first filter cake is yet to be made. Naturally it will be impossible to get any operating data about it, but we are rather fortunate in having with us the gentleman who will be in charge of the operation at Republic Steel. During the past week or so the tanks have been filling up and I doubt whether Mr. Morgan was able to see any cake from the installation, but I think we would all appreciate having him give us a few comments on the installation so far as he has seen it up to date.

M. F. MORGAN,† Youngstown, Ohio.—We have installed two 70-ft. tanks with a new type of Dorr classifier or thickener. We are a little unique, having our tanks above the ground. From an operating man's standpoint, the tunnel and the discharge to the suction pump have always been a bone of contention and really an evil in the way of handling sludge material. Our tunnels are 6 ft. high and 6 ft. wide, and there are two outlets from each tank. We first start with 8-in. pipe and 8-in. valves on that installation, and then it is reduced to the 2½-in. pipe to the sludge pumps, so that if something should get into the tank we have a way of shutting it off and taking out the pipe in between the reducer and taking out the foreign matter without emptying the sludge tank.

We have installed the American type filter, six disks, in the sintering plant proper, and are discharging onto a 30-in. belt. In other words, we are not crowding our

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\* Vice-president, Arthur G. McKee & Co.

sludge material down to a small opening and getting it in large gobs. What we are trying to do is to have the smallest amount possible of filter cake to take care of in the sinter mix and use the amount of flue dust that is going to come into the tanks from a four-furnace operation, so that it will not affect our sintering operation.

This material will discharge directly onto a collecting belt going up to the pug mill and from there right to the sintering machine. If the sintering plant should be down for a considerable length of time, there is an auxiliary conveyer that will carry the material to the ore yard to be used at a future time. Our tanks are concrete and our pumphouse is brick. Everything is about as near perfect as we could possibly have it, and we are expecting not only wonderful results but a really clean installation, and the problem of handling the sludge is, of course, overcome by operating the sintering plant 24 hr. a day seven days a week.

We are very proud of it, and we think we really have a Dorr installation with which we will not have mud, etc., all around. We look for no trouble whatsoever; and, of course, hope we will not have any.

W. A. HAVEN.—Mr. Morgan, it is not often we get an opportunity to combine some of the essential features of two very important subjects, flue-dust recovery in the form of sludge and conversion of that sludge into a usable blast-furnace raw material. As most operators know, Mr. Morgan has had perhaps as broad an experience as anyone in the country in the art of sintering flue dust. I wonder if you would be kind enough to give us the benefit of your opinion as to the best way of adapting sludge to the operation of a sintering plant.

M. F. MORGAN.—The handling of sludge from the sintering-plant standpoint goes back to what kind of sinter will be made and what it will do in a blast furnace. Sinter for blast-furnace use has been studied carefully, especially in the last few years—the types of sinter that are fit for the blast furnace and the types that are not. We have found from actual experiments that it takes a sinter that is of uniform quality. In handling a sludge material with 30 per cent moisture there must be enough carbon in that material not only to dry out the moisture but also to congeal it into a sinter cake. The moisture will vary, and it is a difficult material to handle, which will go into—well, gobs or balls—and in order that the air may pass through the charge and burn the carbon, a very peculiar structure of sinter is obtained by handling the filter cake alone or a very hard sinter and very low tonnage and high cost of operation.

We feel that the smallest amount of the wet sludge that can be added with the flue dust and mixture will give the best results. I am not in favor of sintering flue dust alone. I think a sinter plant should have carbon control just as the blast furnace has carbon control, and it cannot be done with flue dust alone; therefore, adding some ore to the mixture along with the flue dust will make an ideal sintering mixture. We expect our wet sludge to replace ore in the mixture to a certain extent.

This is also tentative, but what we are aiming to do is to hold a uniform quality of sinter 24 hr. a day, so that the furnaces will receive the same kind of sinter day in and day out. I think, from my personal experience, that when sinter starts to vary in quality it is going to show a variation in blast-furnace practice. I think that every blast-furnace superintendent knows the kind of sinter that he wants, therefore everything depends entirely upon the operator of the blast furnace as to what kind of sinter is made.

We handled the sludge in Youngstown by putting it into gondola cars and taking it to the stock pile of flue dust. The current run flue dust is also dumped into the stock pile, and we mix it, one grab bucket of sludge to two grab buckets of dry catcher dust. It slides down over the pile in a wet form. The large gobs of dust fall to the end of the flue dust pile, and we keep picking that up until we have reduced the moisture in the sludge with the dry dust to a point at which we can sinter it in the sintering plant without any trouble.

It is just a matter of reducing the moisture, but in adding wet sludge to the sintering plant, I believe that the thing to do is to get it over the entire period of operation and in as small doses as possible, because it is very fine and it is a very hard product to handle alone.

W. A. HAVEN.—What do you consider is the maximum percentage of sludge you can use with flue dust and make a good sinter?

M. F. MORGAN.—That would depend entirely upon the size of sintering plant and also on the amount that must be handled. We expect to handle between 100 and 125 tons in 24 hr. on a plant capacity of 400 tons in Cleveland, and we think we are going to do it without any trouble whatsoever, but I do not think there is any limit to the amount. It depends upon how long it is sintered, how much carbon is put into the mixture and the class of sinter required.

W. A. HAVEN.—That is a good answer. In other words, you could sinter all sludge if you had to?

M. F. MORGAN.—Yes.

R. C. ALLEN,\* Cleveland, Ohio.—I think that something ought to be said from the standpoint of the iron ore men. It was remarked that Mr. Counselman is a nuisance to blast-furnace people. It has occurred to me that in the same sense he is also a nuisance to iron ore people. For although it is true that Mr. Counselman teaches the miner by use of his gadgets to recover the maximum of iron from mill heads and to use successfully leaner and leaner mill heads, thus adding greatly to the available reserve of iron ore, he also is teaching the furnaceman how to make pig iron with the use of a minimum amount of iron ore. What he gives to the miner with the one hand he takes away with the other. He is a practical conservationist. Conservation is good for everybody in the long run but many oxen are to be gored in the commercial adjustments that follow in its wake. Just now we have a superabundance of iron ore seeking a market and would be pleased even if astounded to hear of plans for using more virgin metal in making iron and steel.

The furnaceman and the miner have much, but not everything, in common. By experience we know that when things go wrong at the furnace the ore people are almost sure to be involved before the trouble shooting has found its mark.

I am reminded of an experience with Chairman Haven some years ago when he was an operator of blast furnaces. He is now a builder of furnaces. Mr. Haven found zinc in his furnace and traced its source to an ore that had been obtained from us. My first reaction to that information was that he was getting something he was not paying for, but that did not make a hit with him because he did not see how he could make spelter in a blast furnace. It occurred to me then that if zinc were in that ore probably other elements not accounted for in the ordinary commercial analysis were there too. And so it proved. Mr. Charles Murray made a complete analysis and found not only zinc, as determined by Mr. Haven, but also lead, silver and cobalt.

In the iron-ore business—and probably in the steel business—we do not really analyze the materials that we are using. I have often talked to Mr. Murray and others interested in the composition of ores about the interest that would attach to a detailed study of iron ore to find out what it is and what it actually contains.

I do not remember, Mr. Haven, just how that argument came out. I believe that you went on using the iron ore.

W. A. HAVEN.—That is right, we did. We had an awfully hard time finding that zinc—we analyzed scrap and everything else—because Mr. Murray's analysis

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\* Vice-president, Oglebay Norton & Co.

did not show any zinc, as you have said. However, we knew we were getting zinc because we were finding it in nuggets in the linings and it had to come from some place. The chief chemist there was challenged by the problem and got samples of all the ores, big tubfuls, and boiled it down repeatedly until finally he found the zinc. There is just this much to be said about my complaint, Mr. Allen. I was interested in your admitting it here, but I wish you would tell them that I never told anybody but you about it.

R. C. ALLEN.—That is right.

J. T. MACKENZIE,\* Birmingham, Ala.—I should like to ask whether the zinc concentrates in the flue dust and whether those volatile materials will build up to still more troublesome concentrations with these different things.

W. A. HAVEN.—I do not know where that zinc does finally go. It goes out in such small quantities that it is hard to find. It is only in the furnace itself where it is being volatilized and then condensed and going up and down like a pump handle that finally there is a concentration of the zinc gases that enables it to be precipitated in quantity—and that would not be serious if it were not for the fact that some of us believe that in condensing out and crystallizing in the lining it has a bearing on disintegration of brick. There is some question as to whether we are right or wrong about that; but the fact of the matter is that we could find nuggets of zinc in our lining and some had split shells along with it.

As to concentration in flue dust, it is my own opinion that it leaks out in small quantities, because in the ordinary blast furnace we had to take barrels of it to find it to start with.

F. B. THACHER,† Chicago, Ill.—I do not believe very much zinc gets out of the furnace. I think it practically all condenses back and is dissipated either in or through the lining some place. You might get it out the top of the furnace and into the dust if you had high top heats, but I do not think the modern blast furnace has a sufficient top heat to let it go out as a volatile. It practically all condenses before it gets up to the top of the stack.

R. C. ALLEN.—I think that a study of the composition of iron ore could be undertaken by this committee. Iron ore from the Lake Superior region is analyzed only for its major constituents, but there are elements in the ore that the miner and the blast-furnace man do not know anything about. I suspect that there are very few iron ores that have ever been completely analyzed. Would it not be well worth while for this committee to undertake a serious study of the composition of iron ore? I do not know what all of the implications would be, but certainly we are entitled to know about the ore we are using, not only its gross characteristics but all of its characteristics. It seems to me that this is the proper organization to undertake that study. I am personally much interested in such an investigation; I should like to hear from Mr. Murray about it.

C. B. MURRAY,‡ Cleveland, Ohio.—In the last year or two we have made analyses of certain ores particularly as to chromium, and we find chromium in practically all of the Lake Superior ores. Only one ore went as high as 0.2 per cent. Most of them have chromium in the second and third decimal place. Whether that is a detriment to the ore, I am not prepared to say. We have also analyzed all the ores for zinc, and with one exception they all have zinc, mostly in the second and third decimal place. That is as far as I have looked into these things.

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\* Metallurgist and Chief Chemist, American Cast Iron Pipe Co.

† Assistant General Manager, Interlake Iron Corporation.

‡ Crowell & Murray.

W. A. HAVEN.—Before we leave this subject I am going to ask your patience to tell you about somebody spoofing me or trying to spoof me recently down in southern Ohio. There they have a peculiar operation. They dredge their limestone out of the river—actually have a limestone gravel, the most interesting thing I have ever seen in limestone. Somebody, in analyzing the limestone, found a small quantity of gold. Somebody tried to lead me to believe that when they took the salamander out of the furnace when they shut it down they were going to pay for the whole rebuilding with what they got out of the bottom of the furnace.

What would happen to gold charged into a blast furnace in small quantities? Where would it eventually show up, if at all?

J. S. UNGER, Pittsburgh, Pa.—In one of the first books published in Germany by Dr. Fresenius, who was one of the fathers of analytical chemistry, he shows a complete analysis of a pig iron in which he gives a certain amount of silver and gold. If it had not been for the authority he possesses, as an analyst, I would be inclined to believe that a fairy story. I do not think Dr. Fresenius would publish anything that he himself actually had not determined by analysis.

It is possible, and I think it is correct, that if you take a large sample you can find gold and silver in limestone or iron ore. Following the discussion, zinc, as you know, is quite common in some ores, sometimes in very large quantities, as in some of the manganese-iron-ore-zinc ores of Pennsylvania. Whether zinc is injurious to the quality of pig iron made is a question of doubt. If an ore carried small quantities of zinc, the zinc might be volatilized and carried over and condensed as a metallic zinc, or it might be oxidized and go up through the burden in the furnace as a fume, and if carried through as a fume, as oxidized zinc, it probably would be mixed with the flue dust. The likelihood is that the zinc would be found in the flue dust and not with the pig iron.

## The Freezing of Cast Iron

By ALFRED BOYLES,\* MEMBER A.I.M.E.

(New York Meeting, February, 1937)

"HEREDITY"<sup>1</sup> in cast iron has been a subject of much discussion. Numerous experimenters have found that the properties of gray iron may vary greatly without corresponding variations in composition or thermal treatment. The main structural difference in such cases is in the size and distribution of the graphite flakes and the explanations given usually attribute this difference to some chemical element not shown by ordinary analysis or to some physical factor, such as inclusions in the melt. It cannot be said that any of these theories is completely satisfactory. Much remains to be learned about cast iron and for this reason a study of the material was undertaken as a part of the program of fundamental research at Battelle Memorial Institute. A review of the literature indicated that very little systematic work had been done on the mechanism of freezing in cast iron. The experiments described below are largely concerned with that problem.

### NORMAL AND "DENDRITIC" CAST IRON

As examples of variation in type of structure, photomicrographs of two test bars of cast iron are shown (Figs. 1 and 2) and the composition and properties are given in Table 1. Both are common, unalloyed gray iron.

TABLE 1.—*Composition and Physical Properties of Test Bars*

Test Bar No.	Composition, Per Cent					Tensile Strength, Lb. per Sq. In.	Brinell Hardness
	Total C	Si	Mn	P	S		
13	2.98	2.20	0.79	0.41	0.037	38,500	216
49	3.11	1.70	0.69	0.10	0.030	22,375	200

Test bar No. 13 has normal graphite flakes while No. 49 has very fine, lacy graphite arranged in a dendritic pattern, the matrix in both being pearlite. These two types of cast iron are well known to foundrymen and need no detailed description.

Manuscript received at the office of the Institute Nov. 30, 1936.

\* Metallurgist, Battelle Memorial Institute, Columbus, Ohio.

<sup>1</sup> References are at the end of the paper.



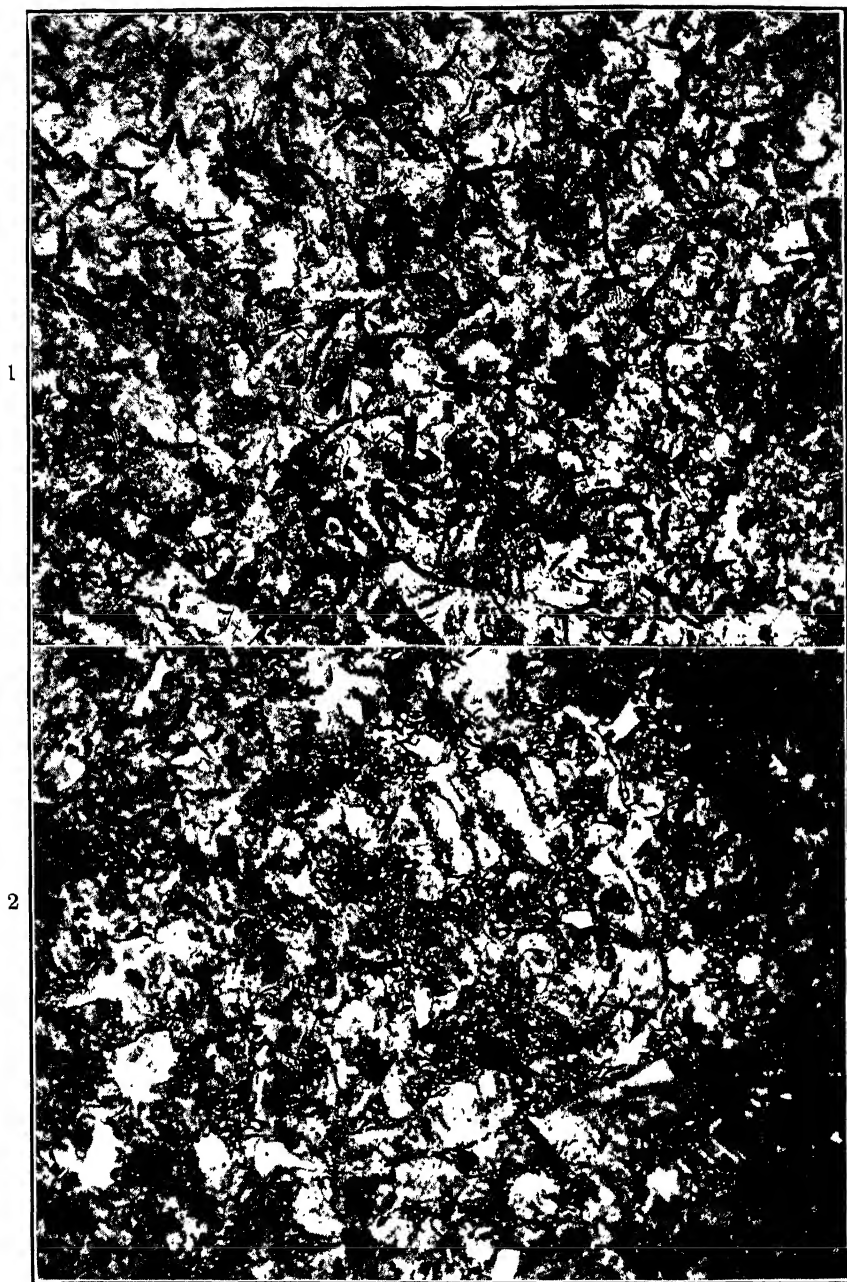


FIG. 1.—TEST BAR NO. 13. NORMAL STRUCTURE.  
FIG. 2.—TEST BAR NO. 49. DENDRITIC STRUCTURE.  
Both etched in  $\text{HNO}_3$ .  $\times 100$ .

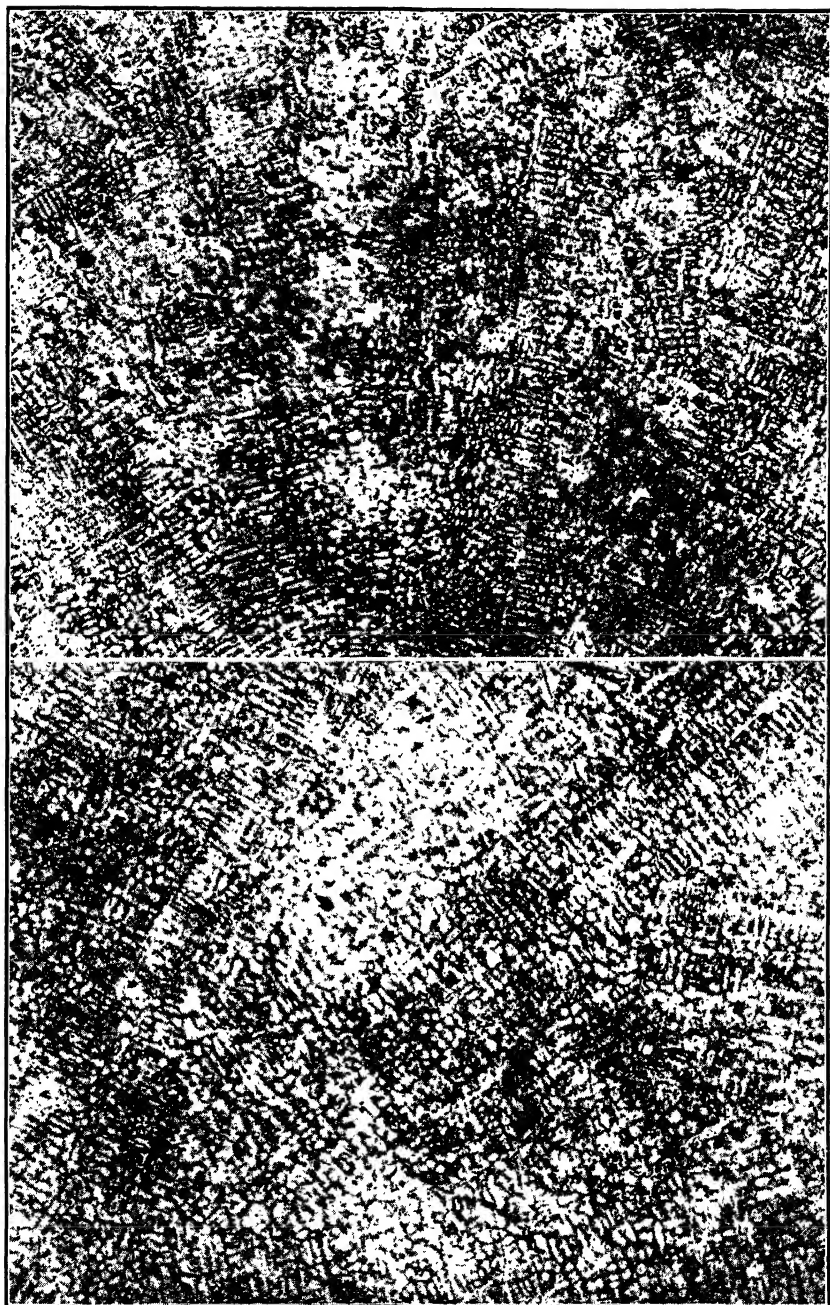


FIG. 3.—TEST BAR NO. 13. NORMAL STRUCTURE.  
FIG. 4.—TEST BAR NO. 49. DENDRITIC STRUCTURE.  
Both heat-tinted.  $\times 20$ .

It was found that by heat-tinting a dendritic pattern could be devel-

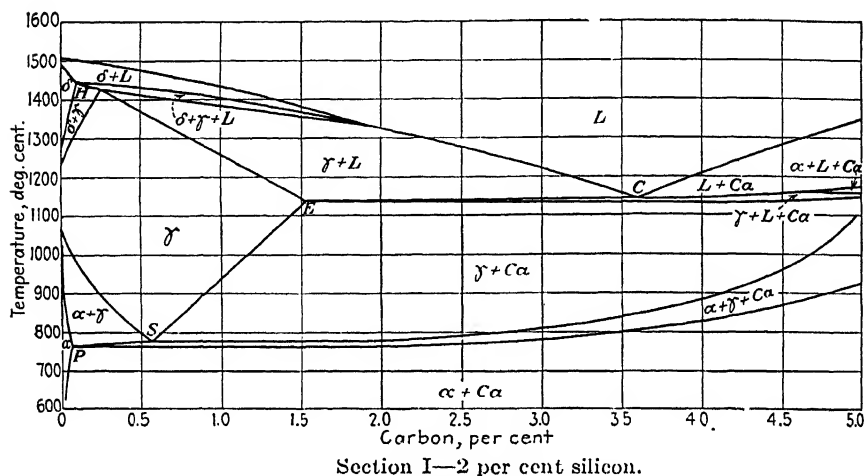


FIG. 5.—CONSTANT-SILICON SECTION OF TERNARY DIAGRAM.  
From Alloys of Iron and Silicon, by Greiner, Marsh and Stoughton.

oped in both samples (Figs. 3 and 4). The operation of heat-tinting consists in slowly heating a highly polished specimen in air until temper colors develop. Portions of the metal that differ in composition produce the series of temper colors at different rates. By stopping the action at the proper time, a color contrast is developed, which reveals the segregation pattern in the metal. Structures developed by etching in the usual way may not show any trace of the pattern revealed by heat-tinting. This method, first employed by Martens and Behrens<sup>2</sup>, is very useful in studying the macrostructure of cast iron.

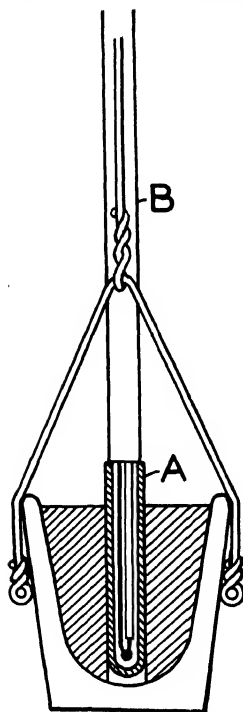


FIG. 6.—QUENCHING ARRANGEMENT.

In Fig. 3 long dendrites are clearly shown, forming a close latticework structure. That these dendrites were the first part to freeze is indicated by the distribution of the phosphide eutectic, which occurs only in the spaces between the dendrites. A close study of the specimen reveals that the graphite flakes are also confined to the spaces between the dendrites. In "dendritic" cast iron this interstitial distribution of graphite is perfectly obvious but with normal flakes a dendritic arrangement is not nearly so apparent (compare Fig. 1 with Fig. 2).

It was thought that something could be learned about the formation of the dendrites by quenching small melts at various

stages of cooling through the freezing range. In an alloy of 3 per cent carbon and 2 per cent silicon the freezing range is rather long (Fig. 5) and a melt while cooling through this temperature interval consists of solid austenite plus liquid. When such a melt is quenched the liquid freezes quickly, breaking up into more austenite plus carbide (which may or may not graphitize). In studying the resulting structure we must be able to distinguish between the austenite that formed during the slow cooling and that which formed during the quench. Two factors assist in making a distinction: (1) a difference in the fineness of their structure due to the great difference in rate of formation; (2) a gradual increase in the amount of primary austenite appearing in samples quenched at successively lower

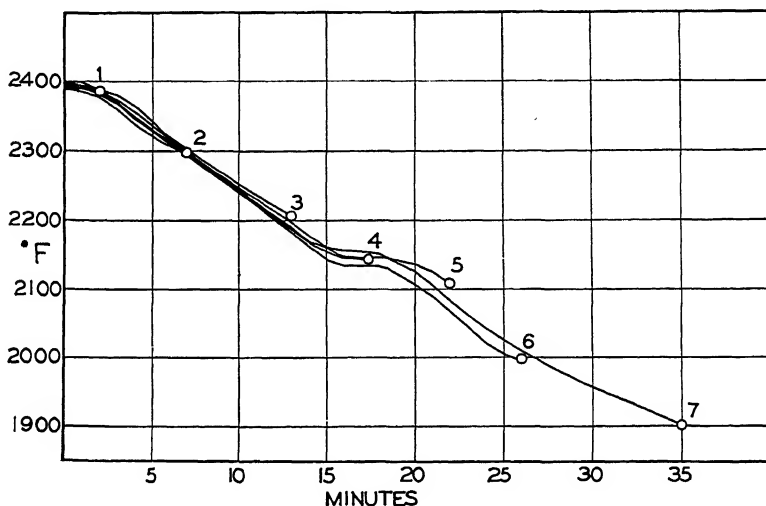
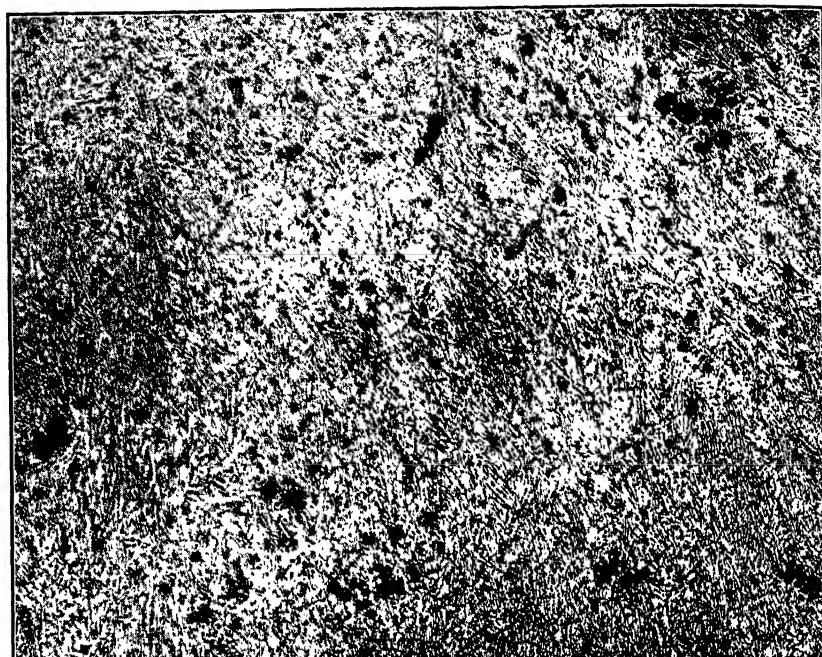


FIG. 7.—COOLING CURVES OF QUENCHED SPECIMENS.

temperatures, a circumstance that should serve to identify the primary constituent.

The method of quenching itself gives still another means of interpreting the results. Small clay crucibles containing the molten cast iron were dropped into water. None of these crucibles broke in quenching and consequently the metal was cooled more rapidly on its top surface than elsewhere. A vertical section through the regulus should show an effect of quenching rate, grading from top to bottom. As an example, a small crucible of hypoeutectic cast iron quenched from the full liquid state will have near its top surface a structure composed of carbide plus what was austenite (transformed of course into martensite). Only a few traces of graphite will be found in this top layer of metal. The amount of graphitization increases toward the bottom of the melt as would be expected. Such graphite occurs as very fine particles arranged in patches, as will be illustrated later.

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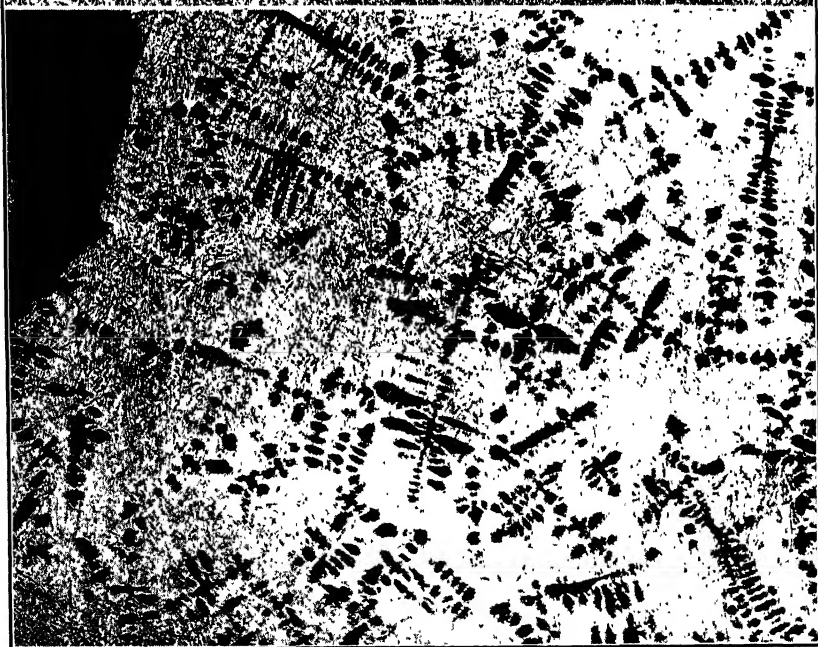


FIG. 8.—SAMPLE No. 1. QUENCHED FROM 2335° F.  
FIG. 9.—SAMPLE No. 2. QUENCHED FROM 2300° F.  
Both heat-tinted.  $\times 20$ .

Obviously, the amount of graphite formed is determined by the stability of the carbide and by the rate of cooling. By comparing different cast irons quenched in the same way, any marked difference in their urge to graphitize may be detected simply by noting the amount of fine graphite in the lower part of the melts. In a melt that is slowly freezing, the parts of the structure already formed at the time of quenching will be uniform from top to bottom, because they are not influenced by the quenching rate. Thus it is possible to distinguish between constituents

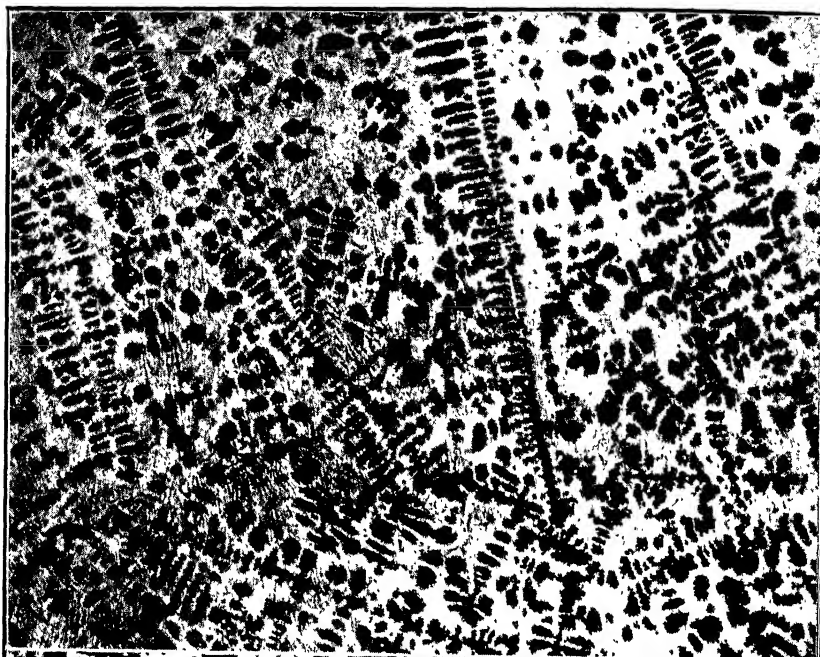


FIG. 10.—DENDRITE OF PRIMARY AUSTENITE PROJECTING OUT OF SURROUNDING LIQUID. HEAT-TINTED.  $\times 250$ .

that existed at the temperature of quenching and those that formed during the quench. A study of a series of specimens handled in this way should give some information on the mechanism of freezing.

Pieces weighing about 50 grams were machined from test bar No. 13 to fit small crucibles (Battersea annealing cups). A short silica tube, A in Fig. 6, was placed in a hole drilled through the center of each charge and into the silica tube a bare platinum-platinum-rhodium thermocouple was introduced. The crucible and its contents were held against the end of the porcelain tube B of the thermocouple by means of a bail of nickel wire. At any time the whole assembly could be dropped away from the thermocouple by releasing a wire attached to the bail. A vertical-tube resistance furnace was used in melting. In each case the melt was brought up to  $2400^{\circ}\text{F}$ ., the power cut off and temperature readings started. After

11



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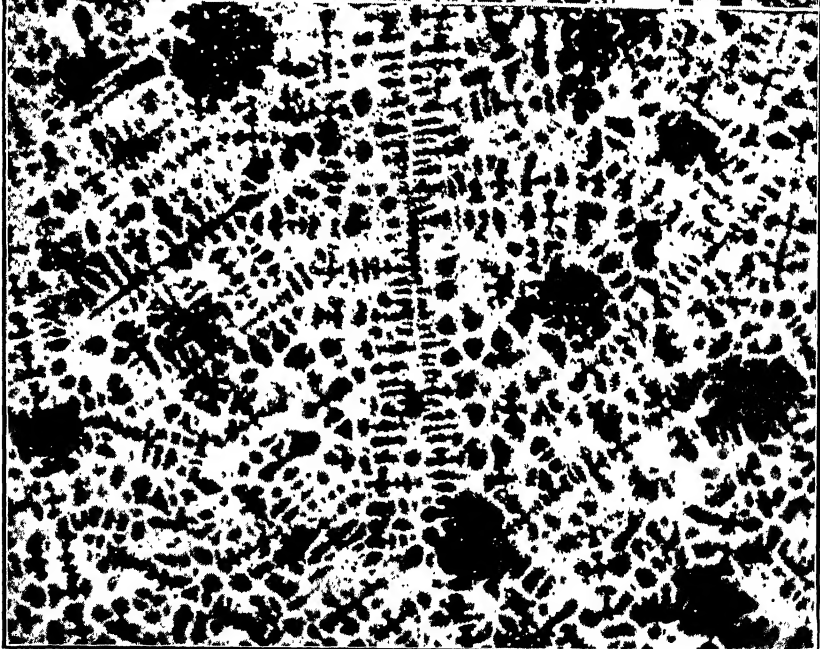
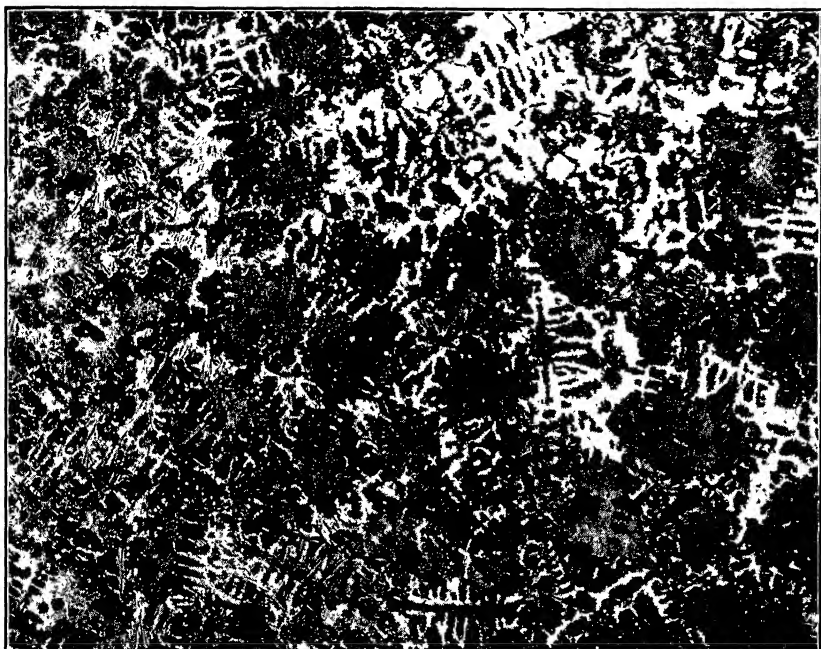


FIG. 11.—SAMPLE No. 3. QUENCHED FROM 2200° F.  
FIG. 12.—SAMPLE No. 4. QUENCHED FROM 2140° F.  
Both heat-tinted.  $\times 20$ .





13



14

FIG. 13.—SAMPLE No. 5. QUENCHED FROM 2110° F.  
FIG. 14.—SAMPLE No. 6. QUENCHED FROM 2000° F.  
Both heat-tinted.  $\times 20$ .



a lag of about two minutes the normal slow cooling began. At the desired temperature the melt was dropped into a vessel of water placed below the furnace. Commercial tank nitrogen was passed through the furnace during melting to keep down oxidation.

Temperature readings were taken at one-minute intervals and are shown plotted in Fig. 7. The quenched samples were sectioned vertically so that the whole structure from top to bottom could be studied. In this way the effect of quenching rate was observed. In describing the samples the constituents of the metallic groundmass will be mentioned first and the relationship of graphite to these constituents described later.

### *Structure of Quenched Specimens*

*Sample No. 1.* Quenched from 2385° F. The primary austenite is just beginning to form and appears as martensitic patches in a complex background resulting from quenching in the liquid state (Fig. 8).

*Samples No. 2.* Quenched from 2300° F. Dendrites of primary austenite are seen growing in the liquid melt (Fig. 9). The size and number of these dendrites is the same from top to bottom. They were present as solid material at the quenching temperature, as indicated in Fig. 10.

*Sample No. 3.* Quenched from 2200° F. The dendrites have grown greatly in length (Fig. 11). They are very uniformly distributed through the melt.

*Sample No. 4.* Quenched from 2140° F. Crystallization centers have appeared in the liquid between the dendrites (Fig. 12), which is now of eutectic composition. The structure shown is quite uniform throughout the melt.

*Sample No. 5.* Quenched from 2110° F. The crystallization centers have developed into a cell-like structure (Fig. 13). Some liquid filling material still remains at the boundaries of these cells.

*Sample No. 6.* Quenched from 2000° F. The cell structure is fully developed (Fig. 14). In this photograph one of the primary dendrites may be seen crossing three separate cells.

*Sample No. 7.* Quenched from 1900° F.

*Sample No. 8.* Quenched from 1800° F.

*Sample No. 9.* Quenched from 1700° F.

These specimens had the same type of structure as that shown in Fig. 14. The white constituent around the cells diminished in amount as the temperature fell.

*Sample No. 10.* Slowly cooled to room temperature. The cell structure remains as above except that the white filling material is gone. Traces of the primary dendrites are clearly shown (Fig. 15). It is interesting to compare Fig. 15 with Fig. 3, showing the original structure of test bar No. 13. The dendrites differ greatly in size, owing to the difference

in rate of cooling. Both samples show a cell structure and in both the phosphide eutectic is located in the boundaries of the cells, a natural result of selective freezing.

In Fig. 16 the exact field of Fig. 15 is shown, etched in nitric acid. There is no sign of dendrites; the structure is that of a normal cast iron. The ferrite areas of Fig. 16 occur at the center of the cells shown in Fig. 15.

#### RELATION OF GRAPHITE TO STRUCTURE

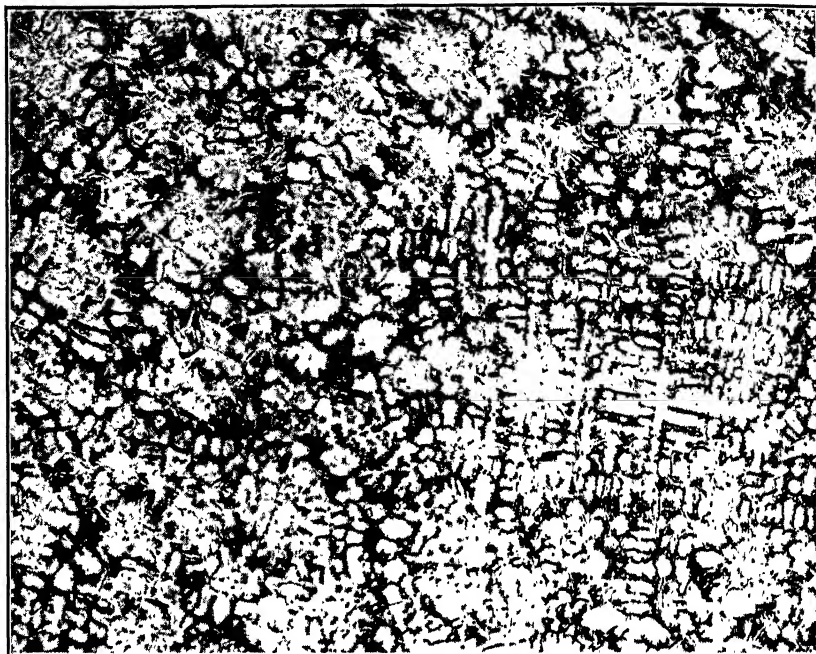
Samples 1, 2 and 3 contain graphite in a very finely divided form, and all contain about the same amount. This graphite occurs only in the filling material between the dendrites and its amount increases from top to bottom in each melt, indicating that it was formed during the quench. The first graphite flakes appear in sample No. 4, quenched from 2140° F. These flakes are confined to the fillings between the dendrites and occur only in the crystallization centers of the eutectic. Some of the flakes appear at the extreme top surface of the melt and the variation in size and amount is very slight from top to bottom. We may assume that they were present as flakes at the time of quenching. With the gradual freezing of the eutectic liquid the flakes increase in number down to the point of complete solidification.

A cast iron containing 0.41 per cent phosphorus is not completely frozen until a temperature of around 1750° F. is reached. As the crystallization centers of the eutectic grow the liquid surrounding them becomes richer in phosphorus, gradually approaching the ternary eutectic of austenite, iron carbide and iron phosphide. According to Künkele<sup>a</sup> a ternary eutectic is always formed in gray iron, which later breaks down into a "pseudobinary" of iron and iron phosphide plus graphite, the extent of the breakdown depending on various factors such as composition and cooling rate. However this may be, it is evident that the presence of phosphorus greatly complicates any study of the way in which the graphite flakes form, the thing in which we are most interested. At the same time phosphorus aids in the interpretation of the quenched specimens by marking out the macrostructure of the metal. A distribution of phosphide like that shown in Fig. 14 is very common in hypoeutectic cast iron. It is sometimes visible in the fracture as a network of fine white lines.

The information derived from this series of quenched specimens may be summarized as follows:

1. Primary austenite freezes out in the form of dendrites, which continue to grow down to the eutectic temperature.
2. Crystallization of the eutectic liquid begins at centers, which grow equally in all directions, forming a cell-like structure.
3. Segregation takes place in two stages: (a) between the primary dendrites and the liquid, (b) from the crystallization centers of the eutectic outward into the boundaries of the cells.

15



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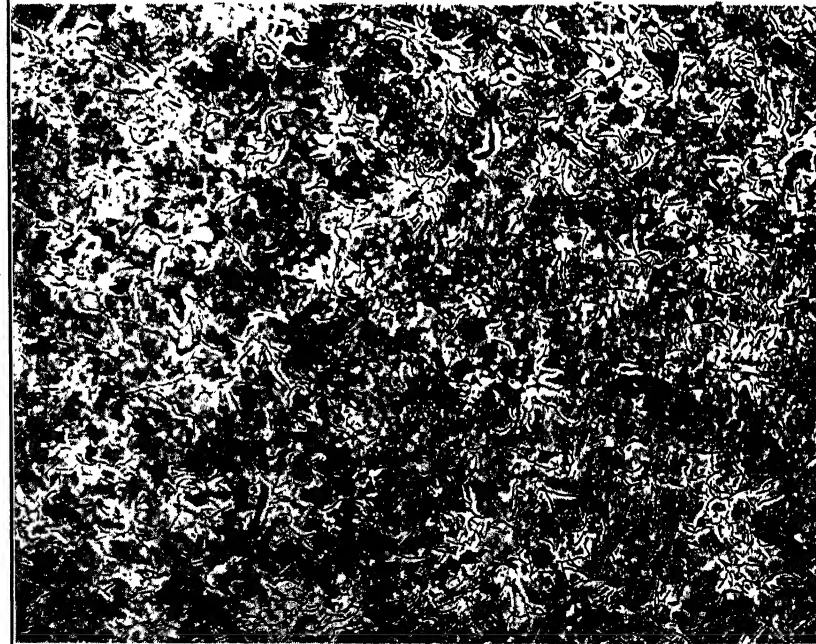


FIG. 15.—SAMPLE NO. 10. SLOW-COOLED TO ROOM TEMPERATURE. HEAT-TINTE  
× 20.

FIG. 16.—SAME FIELD AS FIG. 15. ETCHED IN  $\text{HNO}_3$ . × 20.

4. Constituents formed during the freezing of the eutectic occupy the interstices of the dendrites. The graphite flakes and the phosphide eutectic are thus restricted by the size and distribution of the dendrites.

#### ALLOYS OF IRON, CARBON AND SILICON

In order to study the graphitization of the eutectic without the complication introduced by phosphorus, it was decided to repeat the quenching experiments on an alloy of iron, carbon and silicon made up from very pure materials and having the approximate composition of an ordinary foundry iron. Electrolytic iron (from Westinghouse Electric & Mfg. Co.) was melted with the proper amounts of graphite and silicon carbide to give alloys of the composition shown in Table 2.

TABLE 2.—*Composition of Iron Alloy Test Piece*

Alloy No.	Total C	Si	S	Mn	P
7	3.06	1.91	0.007	Nil	0.010
8	3.49	2.01	0.007	Nil	0.008

The charges were melted in a covered magnesia crucible, using a high-frequency induction furnace. Each melt was sand-cast into two standard transverse test bars 1.2 in. in diameter. Pieces weighing about 50 grams were machined from these bars to fit the small clay crucibles used in quenching. The arrangement shown in Fig. 6 had given trouble by hanging up of the thermocouple and contamination of the platinum by the melt. A different arrangement was made in order to overcome these difficulties. Two thermocouples were first checked against each other. One was then placed in a silica tube immersed in the melt and the other was placed alongside the crucible. Simultaneous readings were taken during the slow cooling of a 50-gram sample of alloy No. 8, with the results shown in Fig. 17. The two couples were again checked against each other and found to agree within 10° over the temperature range in question. In making a quenching test only the couple alongside the crucible was used, care being taken to place the hot junction accurately in the same place with respect to the melt and the walls of the furnace tube. By reference to Fig. 17, the temperature of the metal during cooling could be estimated with a degree of accuracy at least equal to that shown in Fig. 7. Cooling curves were plotted on every melt as a check on the cooling rate down to the temperature of quenching. The results were very concordant.

A new furnace equipped with Globar heating elements (Burrell type B7) was used in these tests and in all subsequent work. The cooling rate of this furnace is much faster than that of the furnace used in the first series of tests (compare Fig. 7 with Fig. 17). Each melt was brought

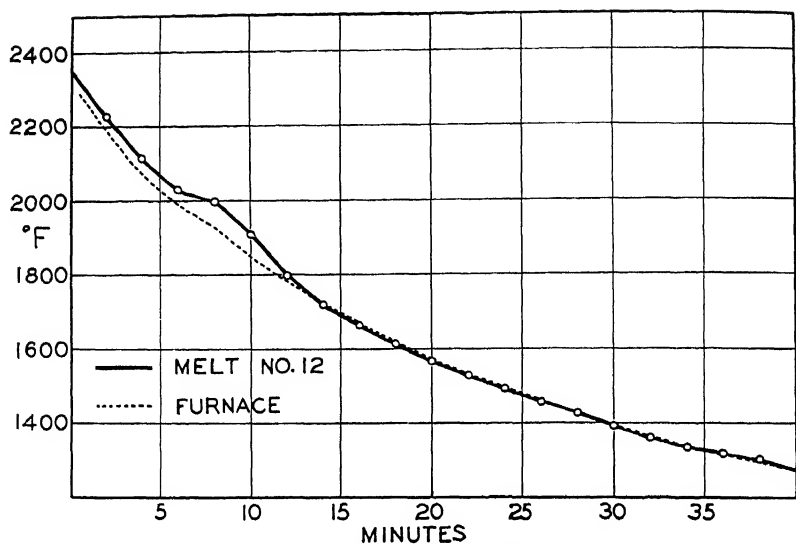


FIG. 17.—COOLING CURVE OF GLOBAR FURNACE AND ALLOY NO. 8.

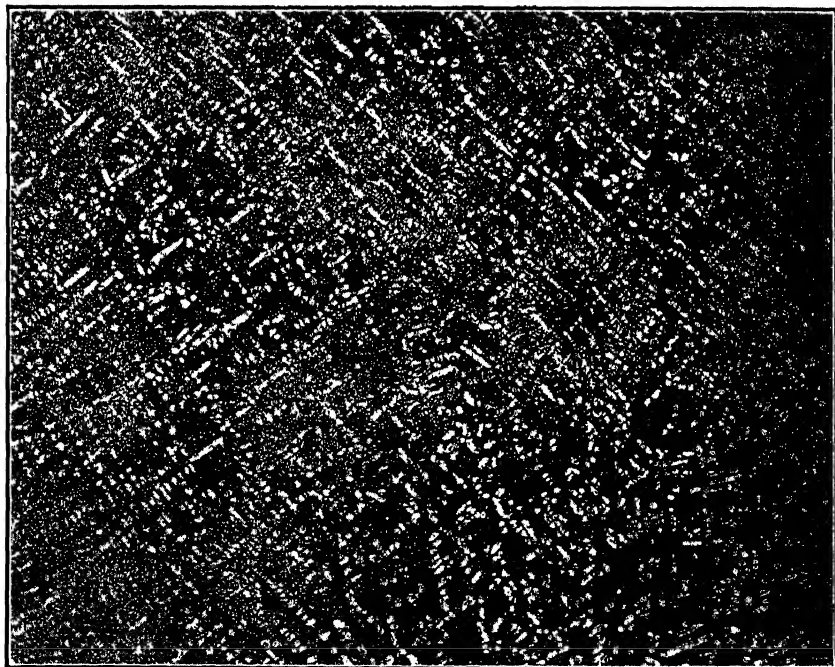


FIG. 18.—TEST BAR CAST FROM ALLOY NO. 8. ETCHED IN  $\text{HNO}_3$ .  $\times 20$ .

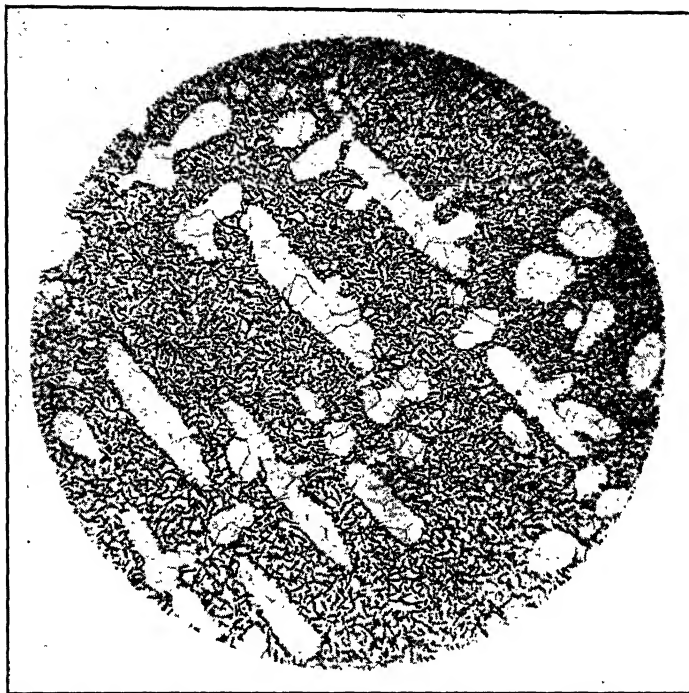


FIG. 19.—DETAIL OF STRUCTURE IN FIG. 18. ETCHED IN  $\text{HNO}_3$ .  $\times 100$ .

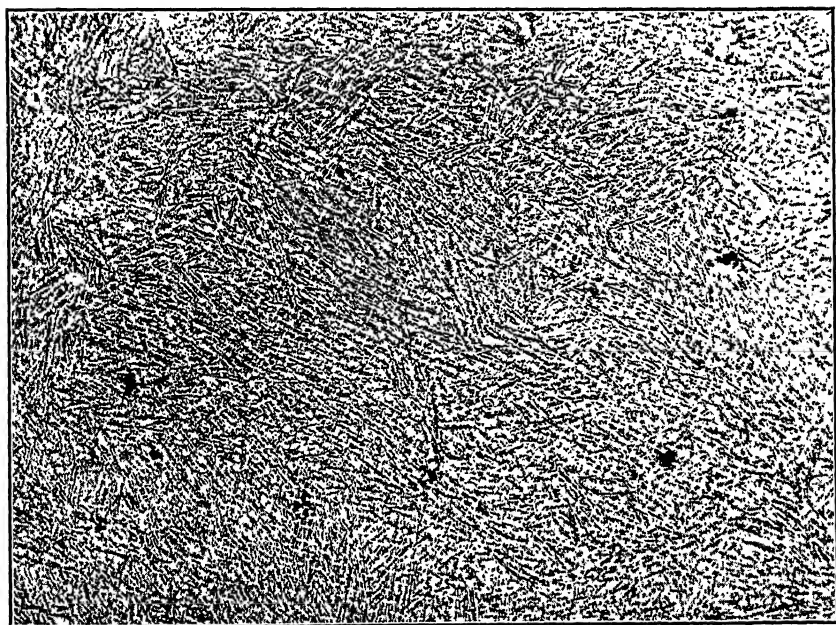


FIG. 20.—SAMPLE No. 16. QUENCHED FROM  $2400^{\circ}\text{F}$ . HEAT-TINTED.  $\times 100$ .

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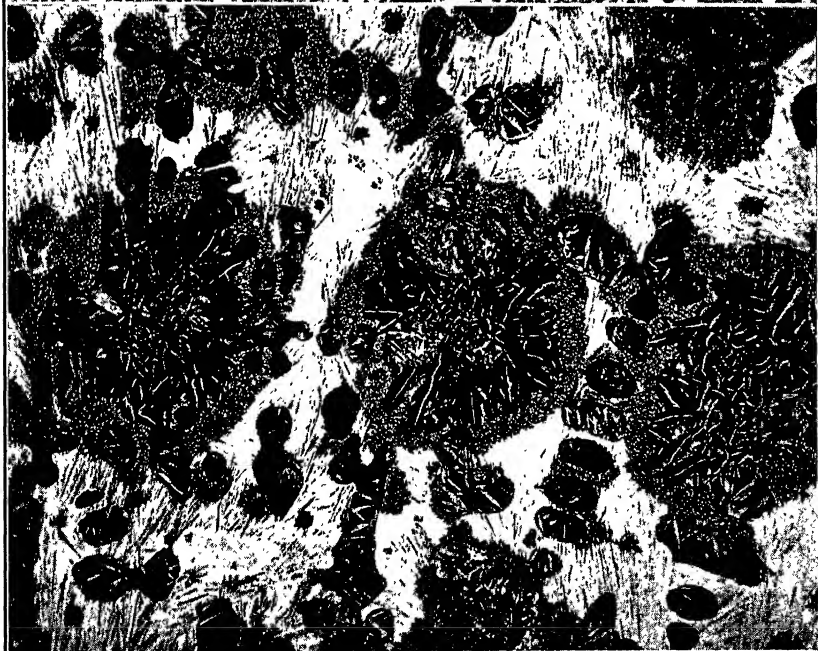


FIG. 21.—SAMPLE No. 18. QUENCHED FROM 2100° F. HEAT-TINTED.  $\times 20$ .  
FIG. 22.—DETAIL OF STRUCTURE IN FIG. 21. HEAT-TINTED.  $\times 100$ .





23



24

FIG. 23.—SAMPLE No. 19. QUENCHED FROM 2025° F. HEAT-TINTED.  $\times 20$ .  
FIG. 24.—DETAIL OF STRUCTURE IN FIG. 23. HEAT-TINTED.  $\times 100$ .



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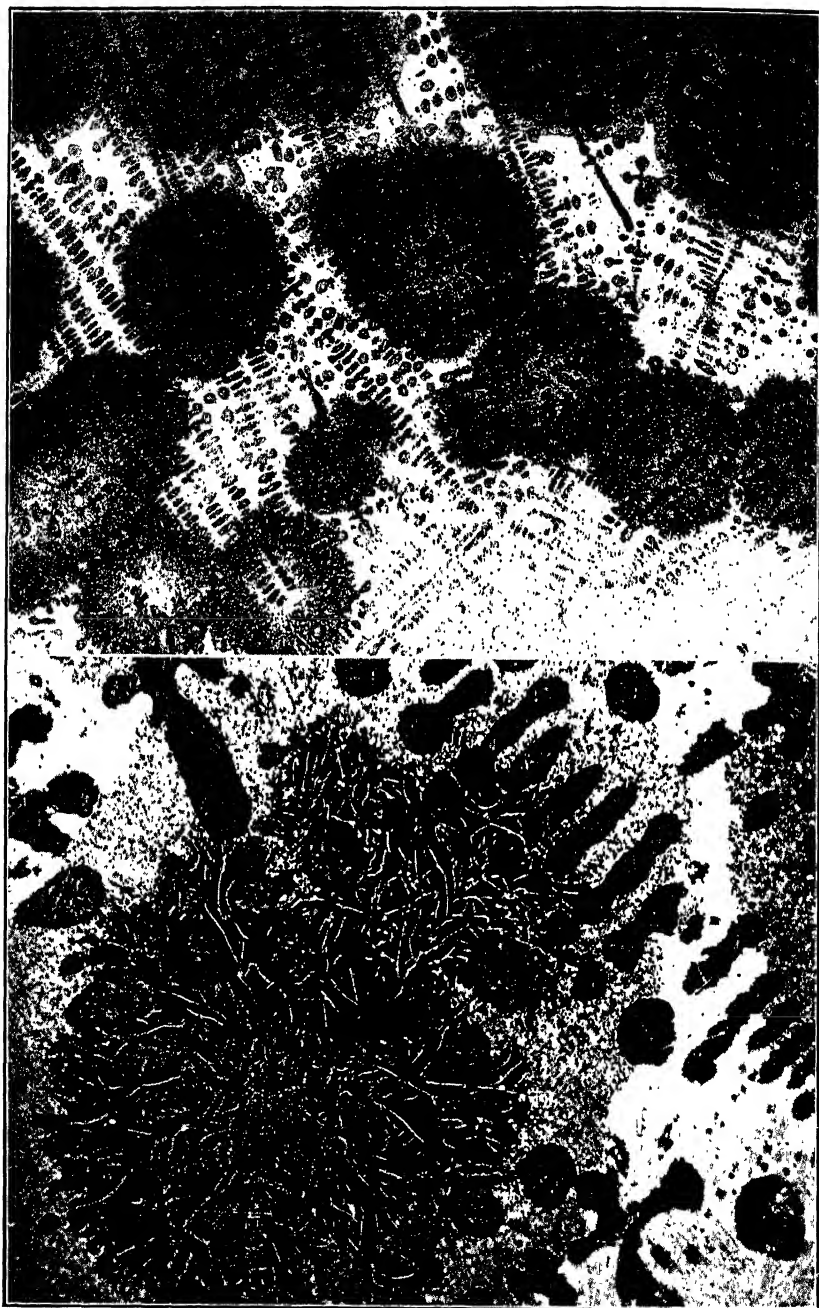


FIG. 25.—SAMPLE No. 20. QUENCHED FROM 2010° F. HEAT-TINTED.  $\times 20$ .  
FIG. 26.—DETAIL OF STRUCTURE IN FIG. 25. HEAT-TINTED.  $\times 100$ .

up at the same rate to a temperature of 2500° F., the power was cut off and temperature readings were started. At the desired temperature the crucible was dropped into water. Commercial tank nitrogen was passed through the furnace during melting.

#### STRUCTURE OF THE QUENCHED SPECIMENS

The structure of alloy No. 8 as cast is shown in Figs. 18 and 19. It consists of ferrite and graphite and is highly dendritic. Rosettes of graphite flakes occur (A in Fig. 18) but most of the graphite is extremely

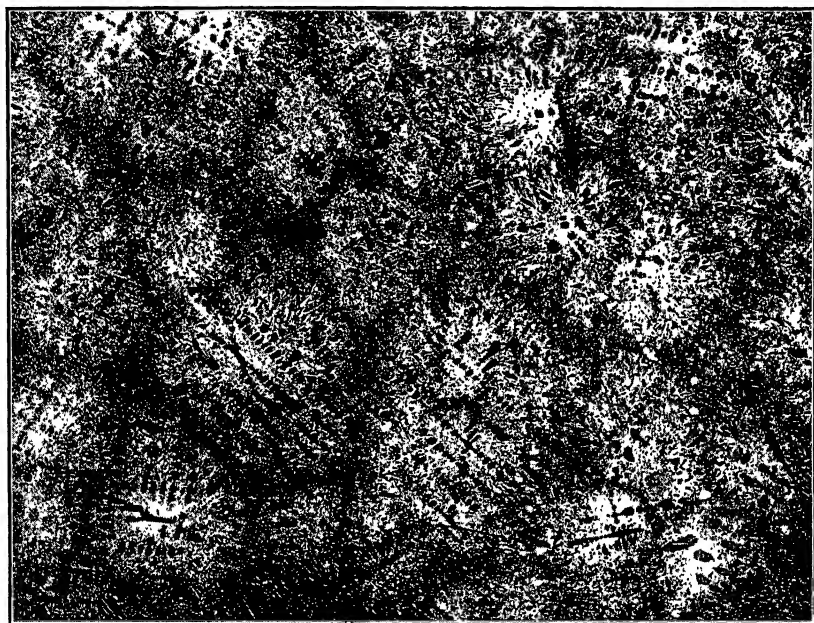


FIG. 27.—SAMPLE NO. 21. QUENCHED FROM 1970° F. HEAT-TINTED.  $\times 20$ .

fine. This metal machined with great ease. The test bars, broken on 18-in. centers, gave a transverse strength of 1950 lb. and a deflection of 0.24 in. The Brinell hardness was 110.

*Sample No. 16.* Quenched from 2400° F. Fig. 20 shows the structure of a small pellet, which ran out into the quenching bath. Graphitization was almost entirely suppressed by the rapid cooling. The metal was fully liquid at time of quenching.

*Sample No. 17.* Quenched from 2200° F. This specimen resembles No. 16. No primary austenite has formed at this temperature.

*Sample No. 18.* Quenched from 2100° F. The metal is just above the eutectic freezing range. Dendrites of primary austenite have formed in the melt, most of which was still liquid at the quenching temperature (Fig. 21). Finely divided graphite occurs in spots (Fig. 22). This

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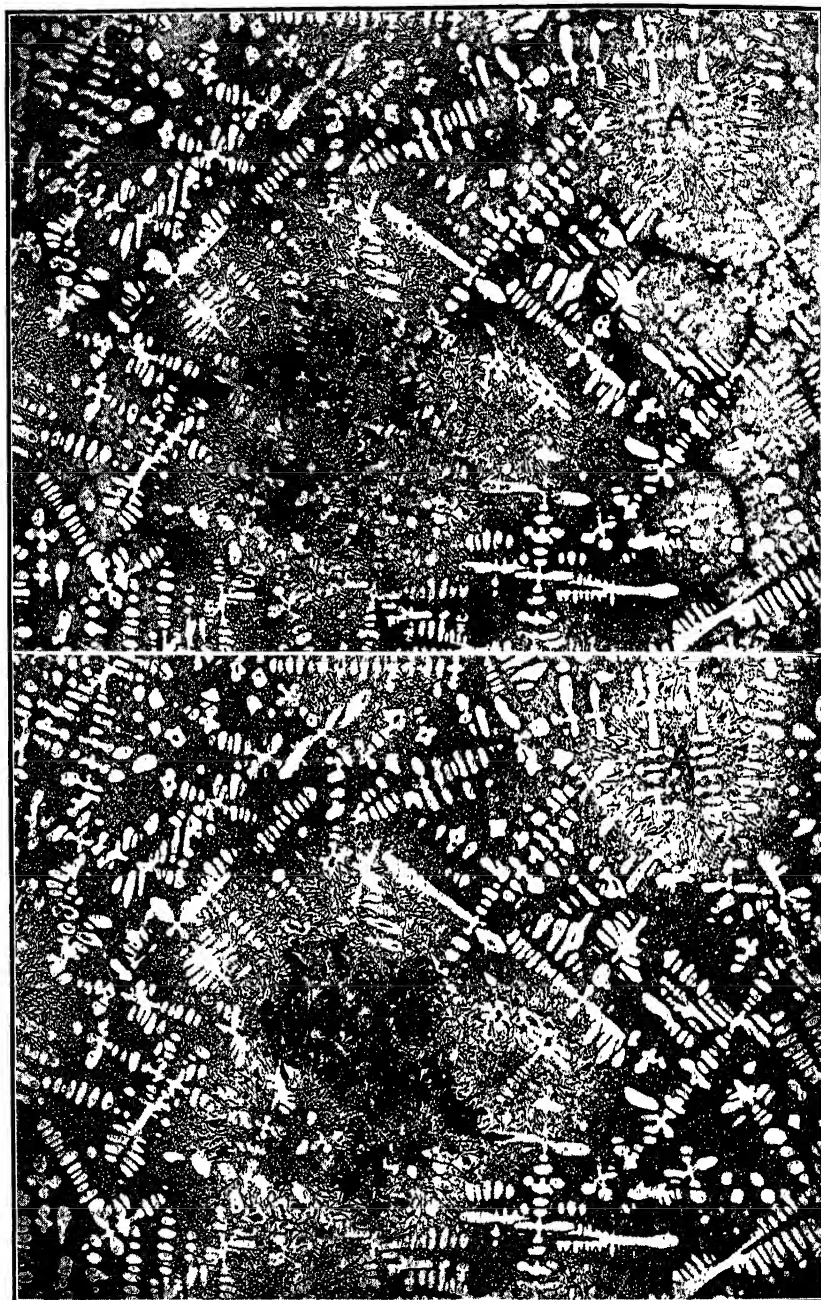


FIG. 28.—SAMPLE No. 23. SLOW-COOLED TO ROOM TEMPERATURE. HEAT-TINTED  
× 20.

FIG. 29.—IDENTICAL FIELD SHOWN IN FIG. 28. ETCHED IN  $\text{HNO}_3$ . × 20.

undoubtedly formed during the quench, since it increases greatly in amount towards the bottom of the melt. Similar fine graphite occurs in the lower part of Nos. 16 and 17.

*Sample No. 19.* Quenched from 2025° F. Crystallization centers have appeared in the eutectic liquid and freezing is under way (Fig. 23). Graphite flakes have already formed in these centers, and additional fine graphite has formed during the quench (Fig. 24). A rosette structure is already apparent around the crystallization centers.

*Sample No. 20.* Quenched from 2010° F. The crystallization centers are closing together to form a cell structure (Fig. 25). A consideration of Figs. 22, 24 and 26 will show definitely that the finely divided graphite surrounding the rosettes formed during the quench. It forms no part of the structure that is slowly developing as the metal cools.

*Sample No. 21.* Quenched from 1970° F. Graphitization of the eutectic is complete. The crystallization centers have developed into a large cell structure (Fig. 27). Rosettes of graphite flakes occupy the large cells. The primary dendrites are clearly visible and appear to be independent of the cell structure.

*Sample No. 22.* Quenched from 1825° F. This specimen is identical to No. 21.

*Sample No. 23.* Slowly cooled to room temperature. This specimen resembles the original test bar. It is highly dendritic and heat-tinting shows a very clear cell structure (Fig. 28) with rosettes of graphite flakes occupying the center of the cells. Fig. 29 shows the identical field of Fig. 28, etched in nitric acid. The matrix is ferrite with a few spots of pearlite like that shown in the center of the field. Etching reveals no trace of the cell structure brought out by heat-tinting.

Several things should be pointed out in Fig. 28 because the whole mechanism of freezing is illustrated in this one photograph. First, the primary dendrites are entirely independent of any other feature in the structure. They were formed first and all that transpired later was confined to the spaces between them. These dendrites are the skeletons of crystals, which were never completed because a new mechanism intervened; namely, the freezing of the eutectic. When the melt reached the eutectic temperature solidification began at various centers, which grew equally in all directions, forming masses of spherical shape (Fig. 25). Graphite flakes formed immediately upon freezing and continued to grow radially as the spheres developed in size. The result is a rosette of graphite flakes centered about each crystallization point. (A typical center is marked *A* in Fig. 28. It should be borne in mind that all the cells shown here are not sectioned through the middle.) The spherical masses finally grew into what might be called the original "grain size" of the eutectic, a thing entirely independent of the size of the primary dendrites.

We are chiefly interested in the size of the graphite flakes because they constitute the most important variable in the structure of cast iron. It is evident in this case that the flake formation is intimately bound up with the growth of the eutectic cells. The first graphite formed at *A* in Fig. 28 was very fine, like that shown in Fig. 19. Radiating out from this are long flakes, which terminate in still more fine graphite located in the boundary of the cell. It is hardly conceivable that the rate of freezing varied in this tiny cell over a range sufficient to account for such a variation in flake size. The mode of formation of the cells suggests rather a connection with selective freezing, since it is reasonably certain that impurities in the eutectic liquid are gradually concentrated into the cell boundaries—as occurred with phosphorus in the freezing of a normal cast iron.

In comparing the iron-carbon-silicon alloy with normal cast iron, several points should be mentioned.

1. The mechanism of freezing is essentially the same in both.
2. The urge to graphitize is much stronger in the iron-carbon-silicon alloy, a thing clearly indicated by the amount of graphite formed in the lower part of melts quenched from the liquid state.
3. The graphite flake structure of the iron-carbon-silicon alloy is highly abnormal and this difference persists after remelting. Since the normal cast iron contains considerable amounts of phosphorus, manganese and sulphur, the question naturally arises as to what influence these elements may have on the formation of graphite flakes.

#### ADDITIONS TO THE IRON-CARBON-SILICON ALLOYS

Additions of phosphorus, manganese and sulphur were made to 50-gram melts of the iron-carbon-silicon alloys with a view to determining the effect of these elements individually. Clay crucibles were used and melting was conducted in an atmosphere of nitrogen. In order to eliminate variables, the melting and cooling cycle was standardized as follows: By controlling the electrical input, the Globar furnace was brought up to 2500° F. in a period of 70 min. and held at this temperature for 10 min., after which the power was cut off and the furnace allowed to cool at its natural rate down to below 500° F. before the melt was removed. Fig. 17 shows the cooling rate.

The most satisfactory means found for making additions was as follows. Several small holes were drilled down into the interior of the charge and the element to be added was placed in the bottom of these holes. Chips taken from the holes were then placed above the added element and driven in very tightly with a punch until the holes were completely filled. Additions were made in the elemental form using materials of reagent quality.

*Effect of Phosphorus.*—Phosphorus did not produce much change in the graphite flakes. The structure of a melt containing 0.48 per cent is shown in Fig. 30. Fine graphite occurs in each crystallization center and short flakes are present in the boundaries of the cells. The matrix is ferrite with a small amount of pearlite, mainly around the phosphide eutectic. Four melts ranging from 0.30 to 0.70 per cent phosphorus gave the same type of structure. In all cases the phosphorus segregated into the boundaries of the cell structure in the same manner observed in cast iron. Otherwise the structures are highly abnormal and bear little resemblance to cast iron.

*Effect of Manganese.*—Additions of Baker's C.P. manganese metal were made to the iron-carbon-silicon alloys to give melts of the analysis given in Table 3.

TABLE 3.—*Iron-carbon-silicon Alloys with Manganese*

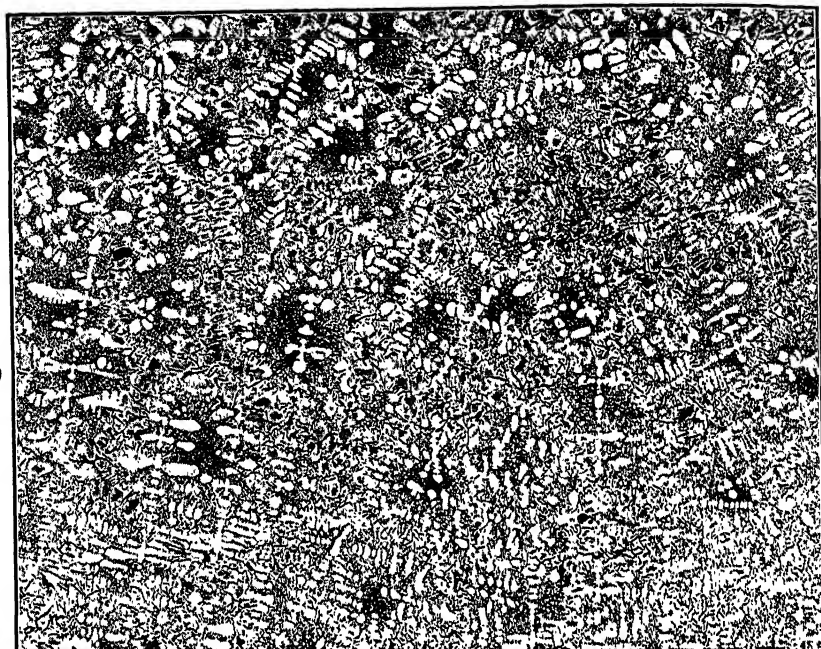
Alloy No. 8, C 3.48 Per Cent, Si 2.01 Per Cent			Alloy No. 7, C 3.06 Per Cent, Si 1.91 Per Cent		
Sample No.	Manganese, Per Cent	Brinell Hardness	Sample No.	Manganese, Per Cent	Brinell Hardness
55	0.15	119	58	0.16	123
57	0.27	110	59	0.35	141
25	0.39	114	60	0.63	156
56	0.73	141	61	0.85	205
45	0.86	179	62	1.22	210

In all cases manganese produced a peculiar type of structure, an example of which is shown in Fig. 31. Fine graphite occurs in each crystallization center in the eutectic. Long flakes radiate from these centers, forming a very pronounced rosette structure. With increasing manganese content the amount of pearlite increases gradually, but even sample No. 62 containing 1.22 per cent is not fully pearlitic. The pearlite occurs chiefly in the boundaries of the cells, as is shown in Fig. 31. These

TABLE 4.—*Iron-carbon-silicon Alloys with Sulphur*

Alloy No. 8, C 3.49 Per Cent, Si 2.01 Per Cent			Alloy No. 7, C 3.06 Per Cent, Si 1.91 Per Cent		
Sample No.	Sulphur, Per Cent	Brinell Hardness	Sample No.	Sulphur, Per Cent	Brinell Hardness
27	0.018	200	46	0.026	216
28	0.024	195	47	0.100	225
24	0.076	190	48	0.146	228
52	0.161	200	49	0.194	228
53	0.250	205	50	0.282	222
54	0.294	205			

30



31

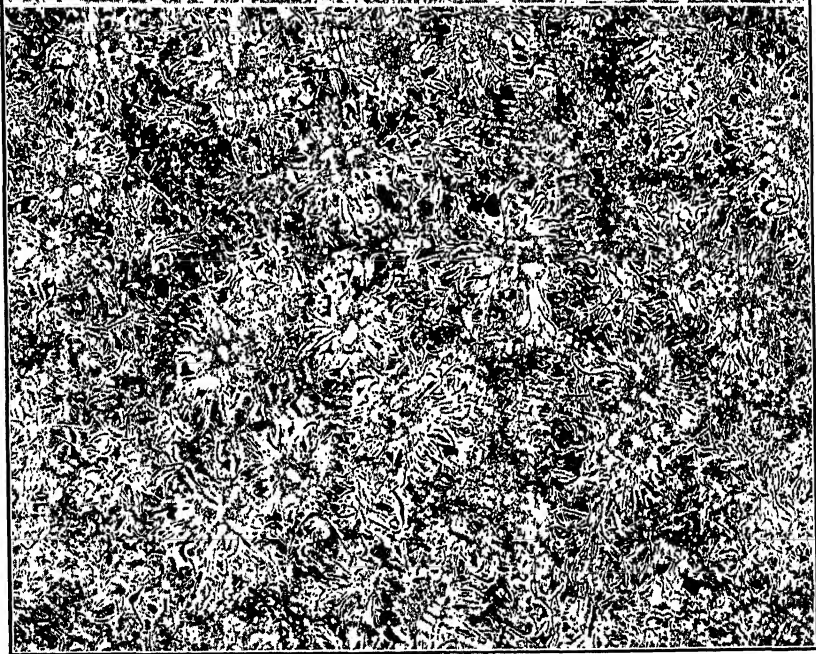
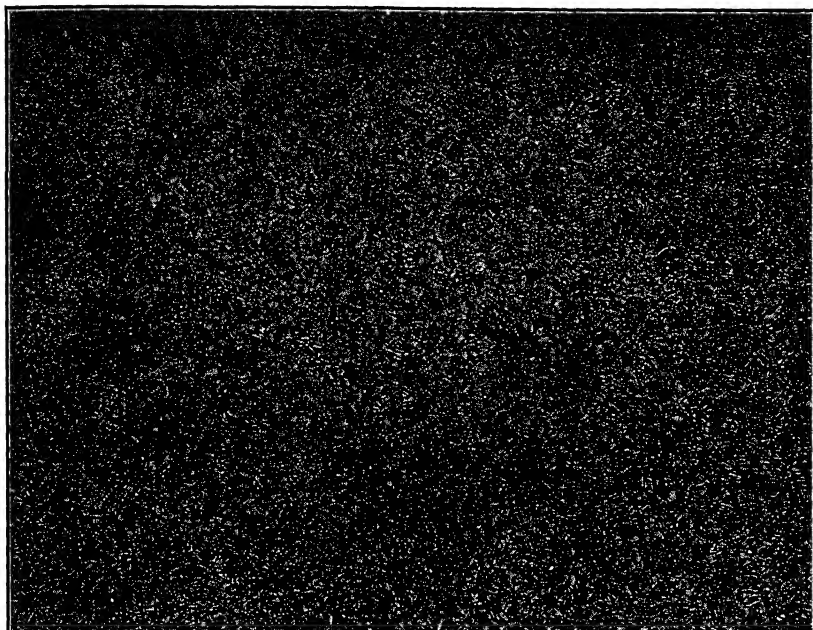


FIG. 30.—ALLOY NO. 8 PLUS 0.48 PER CENT PHOSPHORUS.  
FIG. 31.—ALLOY NO. 8 PLUS 0.39 PER CENT MANGANESE.  
Both etched in  $\text{HNO}_3$ .  $\times 20$ .





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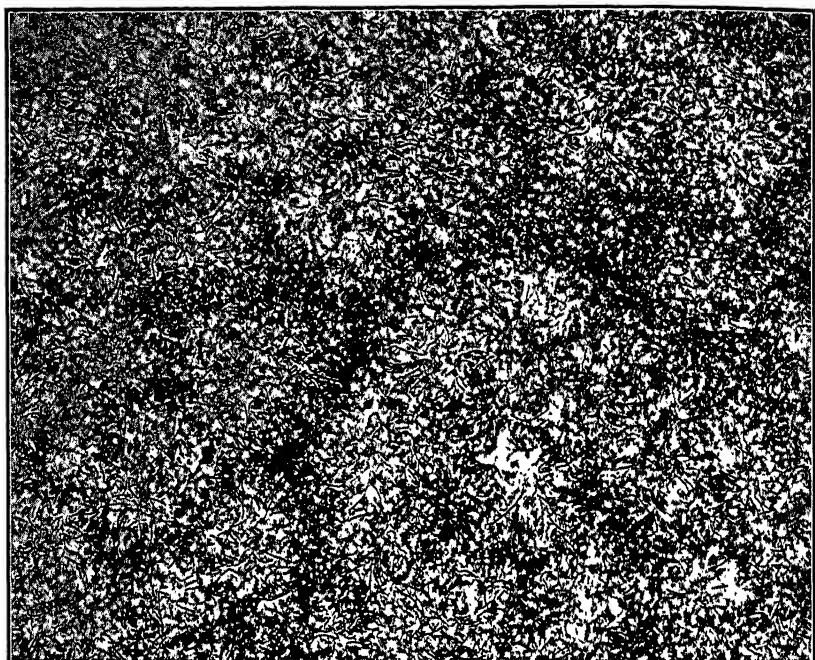


33

FIG. 32.—ALLOY NO. 8 PLUS 0.076 PER CENT SULPHUR. ETCHED IN  $\text{HNO}_3$ .  $\times 20$ .  
FIG. 33.—DETAIL OF STRUCTURE SHOWN IN FIG. 32. ETCHED IN  $\text{HNO}_3$ .  $\times 100$ .



34



35

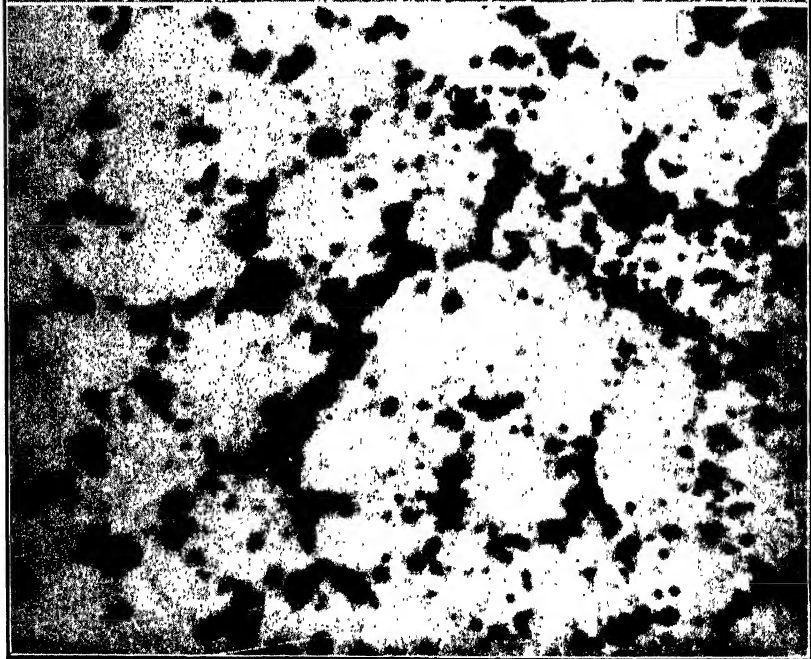
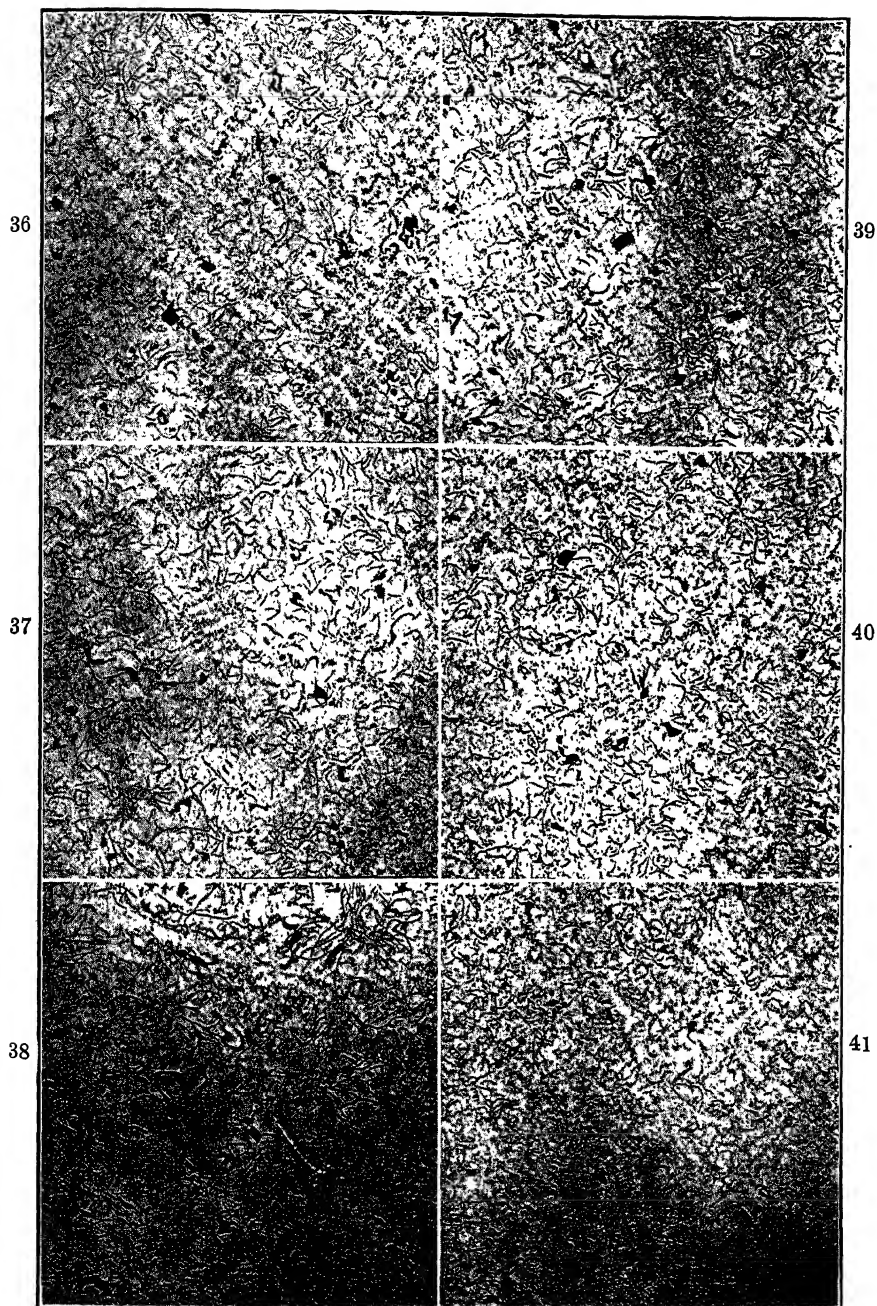


FIG. 34.—IDENTICAL FIELD SHOWN IN FIG. 32. HEAT-TINTED.  $\times 20$ .

FIG. 35.—SULPHUR PRINT FROM SPOT SHOWN IN FIG. 34. ENLARGED 20 DIAMETERS.



FIGS. 36-41.—EFFECT OF SULPHUR ON FLAKE SIZE IN ALLOY NO. 8. UNETCHED.  
× 20.

Per cent sulphur: 0.018, Fig. 36; 0.024, Fig. 37; 0.076, Fig. 38; 0.161, Fig. 39; 0.250, Fig. 40; 0.294, Fig. 41.

42

43



FIG. 42.—ALLOY No. 7 PLUS 0.026 PER CENT SULPHUR. UNETCHED.  $\times 20$ .  
FIG. 43.—ALLOY No. 7 PLUS 0.282 PER CENT SULPHUR. UNETCHED.  $\times 20$ .

structures produced by manganese are quite different from the original alloys (compare Fig. 31 with Fig. 29) but they are also quite different from normal cast iron.

*Effect of Sulphur.*—Additions of elemental sulphur were made to give the compositions listed in Table 4.

The effect of sulphur on the iron-carbon-silicon alloys is very striking. Raising the sulphur to 0.018 per cent rendered the matrix fully pearlitic and produced a very marked change in the graphite flakes. The structure of sample No. 24, containing 0.076 per cent S, is shown in Figs. 32 and 33. It is identical to a normal, fully pearlitic cast iron. Heat-tinting reveals

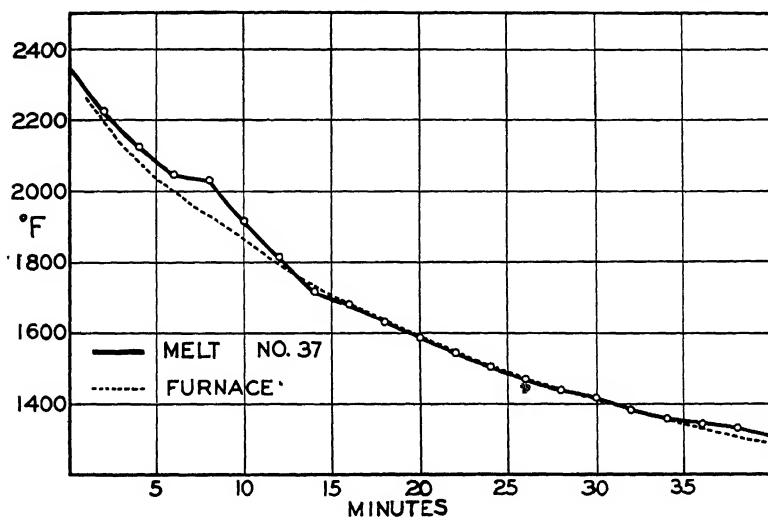


FIG. 44.—COOLING CURVE OF ALLOY NO. 8 PLUS SULPHUR.

the usual cell structure of the eutectic as shown in Fig. 34, which is the same spot shown in Fig. 32. Fig. 35 is a sulphur print from the exact spot shown in Fig. 34. This sulphur print was enlarged 20 diameters and reversed in copying so as to give a direct comparison. It indicates that sulphur has segregated into the boundaries of the cells shown in Fig. 34. All the melts were studied by means of sulphur printing and the same thing was found in all cases. It should be remembered that we are dealing here with the segregation of iron sulphide. In the presence of manganese a different distribution is obtained.

The effect of sulphur on the size of the graphite flakes is illustrated in the series from Fig. 36 to Fig. 41. These photographs show an extremely interesting thing. As the sulphur is raised the flakes increase in size up to a maximum, after which they become smaller again. Exactly the same thing was found in alloy No. 7, with this exception; a given percentage of sulphur exerted a greater effect in the lower carbon material. Such a result is not hard to understand if we consider how the sulphur segregates

during freezing. As the primary dendrites grow sulphur is concentrated into the remaining liquid. The more primary austenite formed, the greater the concentration will be. Dendrites are much more numerous in alloy No. 7 than in alloy No. 8, because of the difference in carbon content. With the same percentage addition, the sulphur content of the eutectic will be higher in alloy No. 7 and consequently the effect on graphitization will be greater.

Fig. 42 shows sample No. 46, made from alloy No. 7 with 0.026 per cent sulphur, which has normal graphite flakes. Sample No. 50, with

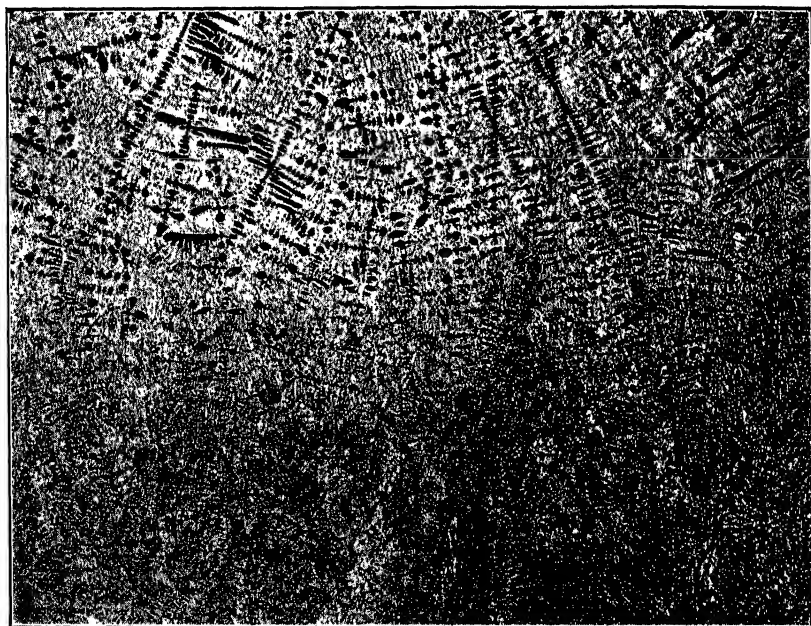


FIG. 45.—SAMPLE NO. 31. QUENCHED FROM 2100° F. HEAT-TINTED.  $\times 20$ .

0.282 per cent sulphur, contains fine graphite, as shown in Fig. 43. In the series between these two there is a gradual transition, the flakes becoming smaller as the sulphur is raised. All the alloys in both series are fully pearlitic, but no trace of mottle could be found, a fact that is borne out by the hardness tests.

#### QUENCHING TESTS ON ALLOY NO. 8 WITH SULPHUR ADDITION

The remarkable change produced by adding sulphur to the iron-carbon-silicon alloys led naturally to a consideration of the effect of sulphur on the mechanism of freezing. By the addition of less than one-tenth of one per cent a highly abnormal alloy is converted into a material having the structure of cast iron. In order to compare the mechanism of freezing in the two cases, quenching tests were made on alloy No. 8

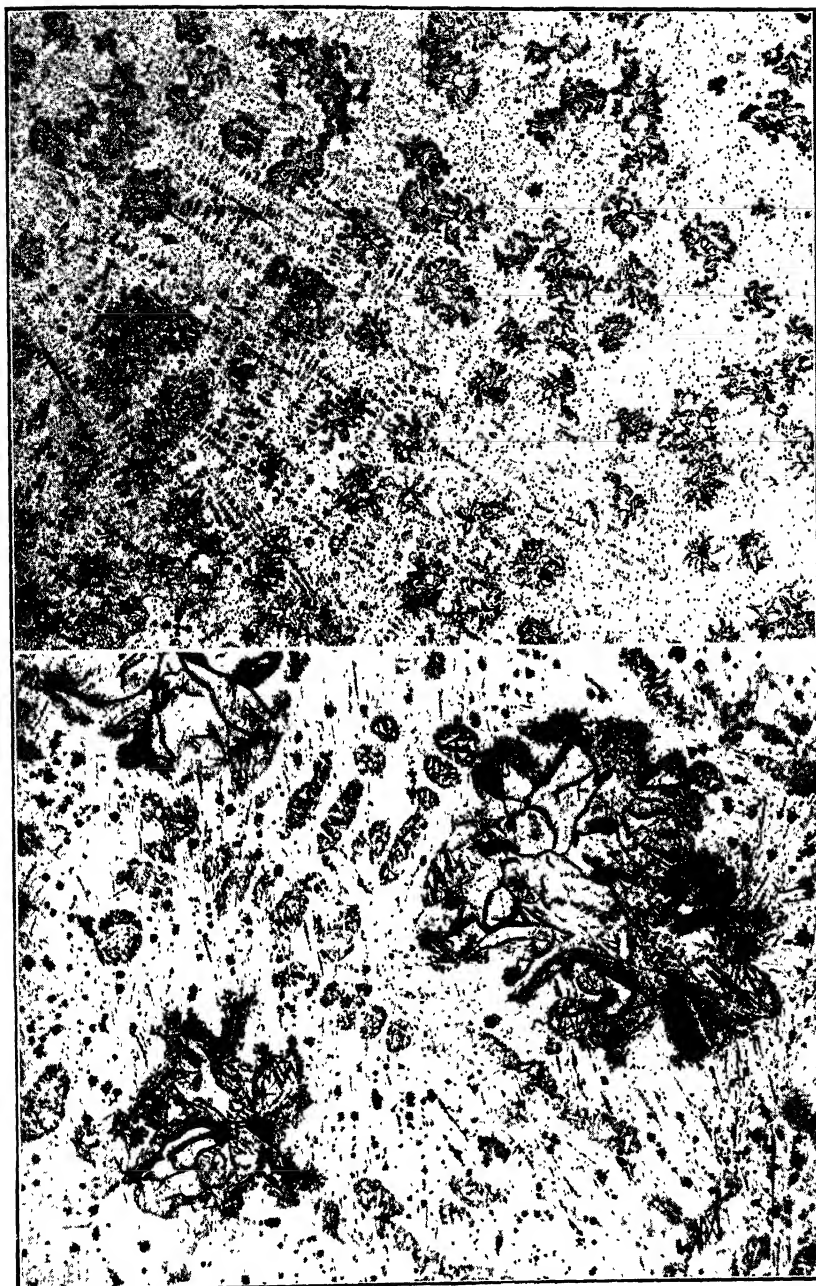
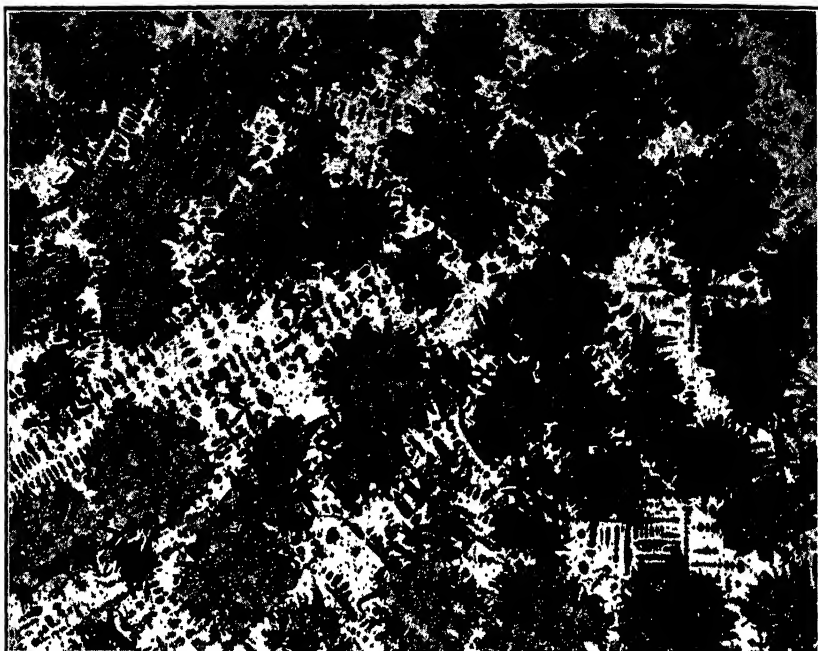


FIG. 46.—SAMPLE NO. 32. QUENCHED FROM 2040° F. HEAT-TINTED.  $\times 20$ .  
FIG. 47.—DETAIL OF STRUCTURE SHOWN IN FIG. 46. HEAT-TINTED.  $\times 100$ .



48



49



FIG. 48.—SAMPLE NO. 36. QUENCHED FROM 2025° F. HEAT-TINTED.  $\times 20$ .  
FIG. 49.—DETAIL OF STRUCTURE OF FIG. 48. HEAT-TINTED.  $\times 100$ .

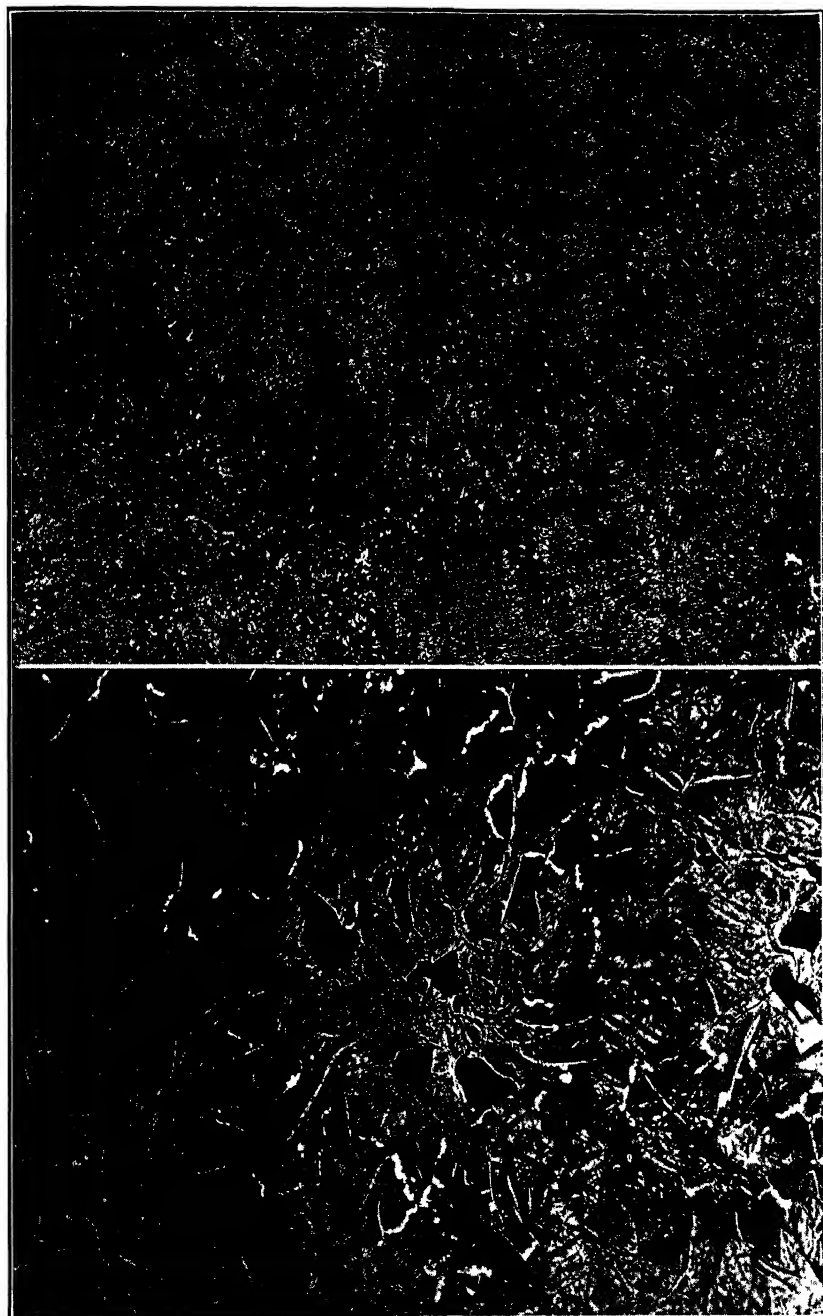


FIG. 50.—SAMPLE No. 33. QUENCHED FROM 1970° F. HEAT-TINTED.  $\times 20$ .  
FIG. 51.—DETAIL OF STRUCTURE OF FIG. 50. HEAT-TINTED.  $\times 100$ .



with a sulphur addition. To each 50-gram charge, 50 mg. of sulphur was added by the method already described. The procedure in melting and quenching was exactly like that used for alloy No. 8. Great care was exercised in controlling the experimental conditions so that the two sets of quenched specimens would be strictly comparable. The structures obtained are described below. Fig. 44 shows the preliminary cooling curves.

*Sample No. 29.* Quenched from 2400° F. This sample is like Fig. 20. At this temperature the metal was fully liquid. Very little graphite formed during the quench.

*Sample No. 30.* Quenched from 2200° F. Resembles No. 29. The precipitation of primary austenite has not started.

*Sample No. 31.* Quenched from 2100° F. Dendrites are growing in the liquid melt (Fig. 45). This structure should be compared to Fig. 21. In the original alloy much fine graphite formed during the quench. The addition of sulphur prevented such graphitization.

*Sample No. 32.* Quenched from 2040° F. Freezing of the eutectic is under way and graphite flakes have already formed in the crystallization centers (Fig. 46). Compare Fig. 47 with Fig. 24. In the original alloy much fine graphite formed during the quench. The addition of sulphur prevented this completely, as is evident in Fig. 47.

*Sample No. 36.* Quenched from 2025° F. The crystallization centers are forming into a cell structure (Fig. 48). Compare Fig. 49 with Fig. 26. The addition of sulphur prevented the formation of fine graphite during the quench. In both cases the graphite flakes are growing lengthwise out into the remaining liquid, but there is a very marked difference in the size of the flakes. A tendency to form rosettes is evident in both cases.

*Sample No. 33.* Quenched from 1970° F. Freezing of the eutectic is complete (Fig. 50). This photograph should be compared to Fig. 27. A little carbide remains undissociated<sup>1</sup> and shows as white areas in Fig. 51. The graphite flake structure is substantially complete at this temperature. Several things should be pointed out in Figs. 50 and 51. The primary dendrites, clearly revealed by heat-tinting, are visible only because they were outlined by segregation during freezing. The austenite which formed during the freezing of the eutectic merged with that of the primary dendrites to give one continuous mass. Upon quenching, this composite austenite transformed into martensite but the markings in the martensitic structure bear no relation whatever to the original dendrites. Etching in the usual way reveals no trace either of dendrites or cell structure. It shows nothing but a matrix of martensite containing normal graphite flakes.

*Sample No. 34.* Quenched from 1825° F. This specimen is identical to No. 33 except that free carbide, like that shown in Fig. 51, is absent. As the alloy cools down below the eutectic temperature additional graphite

will form as the austenite approaches eutectoid composition. Such graphitization is of minor importance as regards the flake structure, because the major features of this structure are already established. The quenching experiments show two things very definitely:

1. Graphite flakes do not begin to form until the eutectic begins to freeze.

2. As soon as the eutectic is completely frozen the flake structure is essentially complete.

A comparison of Fig. 51 with Fig. 33 will illustrate the second point. The quenching tests show further that sulphur has increased the stability of the eutectic carbide as indicated by the amount of graphitization during the quench. The fact that sulphur stabilizes the carbide in cast iron is established beyond dispute. In the iron-carbon-silicon alloys, increasing the carbide stability has increased the size of the graphite flakes, a rather unique behavior.

An effect of this kind suggests a direct relationship between the rate of dissociation of cementite and the size of the resulting graphite flakes. Graphitization, which occurs during the freezing of the eutectic liquid, may be considered as involving two types of action:

1. Liquid  $\rightarrow$  austenite + carbide.
2. Carbide  $\rightarrow$  austenite + graphite.

The first action is governed by the rate of cooling, which was held constant in the experiments under discussion. The second action is governed by the inherent stability of the eutectic carbide, a thing we recognize as variable without knowing just why.

It is evident from the quenched specimens that the flakes grow outward from crystallization centers in the eutectic. As each flake grows, it forms about itself a layer of solid austenite, which is one of the constituents of the eutectic. Fig. 49 shows flakes growing in this manner. Any carbon added to the sides of the flake must diffuse through the layer of solid austenite. Thus we see that most of the growth must occur at one end of the flake, the end that projects out into the remaining liquid. Under such conditions the growth is dependent on two factors; the rate of solidification and the rate at which graphite becomes available. It is not hard to imagine a combination of these factors favorable to the formation of flakes of maximum size.

The number of flakes formed in a rosette depends on the rate at which new centers of graphitization spring up along the advancing front of solidification. The carbide in the liquid surrounding the rosette shown in Fig. 26 was eager to graphitize. Before the flakes shown here could grow to any extent, new centers of graphitization usurped their supply of carbon. The amount of graphite formed during the quench is evidence of this strong tendency for carbide dissociation. In the case of Fig. 49 the urge to graphitize was less intense. With the same rate of cooling,

fewer graphite nuclei formed and each nucleus had a better chance to grow. As a result normal graphite flakes were produced.

In a case where the stability of the carbide is increased still more, the growth of the flakes lags behind the advancing front of solidification. The flakes are pinched off, so to speak, by the freezing up of the metal and as a result small flakes are formed. Such cases are approaching graphitization in the solid state, and the fine graphite so produced differs in appearance from that formed by rapid graphitization, as will be illustrated later. Between the two extremes of very rapid and very slow carbide dissociation, a great range of flake sizes may be produced with the same rate of cooling. Somewhere in this series the flakes will have a maximum size.

The series of structures produced by gradually raising the sulphur content of the iron-carbon-silicon alloys forms the basis for the views outlined above. These are synthetic alloys, produced under laboratory conditions, and it would be unwise to attempt to interpret commercial cast iron in the light of their behavior alone. For this reason an effort was made to study commercial cast iron from the standpoint of rate of graphitization. The problem might be stated in the form of two questions:

1. Does the graphite flake size in ordinary cast iron depend on the stability of the eutectic carbide?
2. If so, why does the carbide stability vary without any significant change in common analysis?

It cannot be denied that the flake size in foundry iron does vary without any marked change in analysis or rate of cooling. The practice of superheating makes use of this fact. Another example is Norbury's<sup>4</sup> process of adding titanium and blowing carbon dioxide through the molten metal. Fig. 52 shows a structure produced by Norbury's method. It consists of a mixture of normal flakes and very fine particles of graphite, the matrix being about half pearlite and half ferrite. Such a structure bears some resemblance to the iron-carbon-silicon alloys (compare Fig. 52 with Fig. 29) and the question arises as to whether the fine graphite in Fig. 52 is due to rapid graphitization. A direct comparison might be made by quenching samples under the same experimental conditions used previously.

It was found that when the metal shown in Fig. 52 was remelted and slow cooled in the Globar furnace it reverted back to a normal structure, the fine graphite disappearing completely. This could hardly be due to a faster rate of cooling in the original casting because Fig. 52 was taken from the center of a cylinder 3 in. in diameter and 6 in. high, cast in green sand. A number of "modified" cast irons were remelted in the same manner and all, without exception, reverted to a normal structure. Obviously, the freezing of such "modified" samples cannot be studied by

means of quenching experiments because the "modified" structure does not survive remelting. Thus an interesting difference exists between "modified" cast iron and alloys of iron, carbon and silicon. In the latter the fine graphite structure is inherent and reappears each time on repeated meltings and freezings.

Such a structure might be looked upon as normal for alloys of iron, carbon and silicon. Hanson<sup>5</sup>, working with alloys of high purity, observed structures closely resembling Fig. 19 in material of similar carbon and silicon content. If we accept this structure as normal, we are forced to consider cast iron as something more than a ternary alloy. The

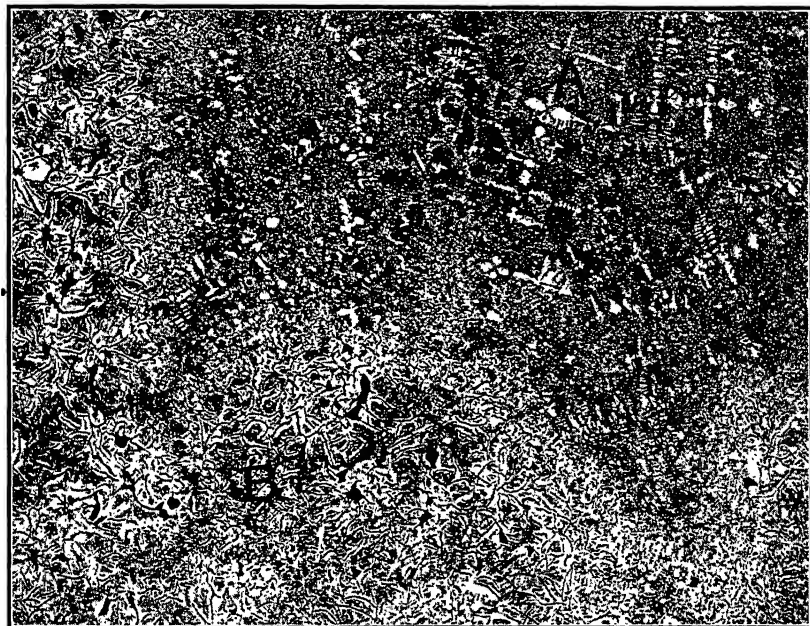


FIG. 52.—CAST IRON MODIFIED BY NORBURY'S PROCESS. ETCHED IN  $\text{HNO}_3$ .  $\times 20$ . C, 3.47 per cent; Si, 2.25, S, 0.028; Mn, 0.68; P, 0.157 per cent. 0.2 per cent titanium added in furnace. Metal blown with  $\text{CO}_2$  for 1 min. in ladle. Poured at  $2600^\circ \text{F}$ .

influence of manganese and sulphur on the ternary alloys suggests that these elements may be basic constituents of cast iron. By simply adding manganese and sulphur to a highly "dendritic" alloy we obtain a perfectly normal cast-iron structure. Examples of this will be shown later. Conversely, it might be possible to convert a normal cast iron into a highly "dendritic" alloy by removing its manganese and sulphur. The mechanism of "modification" is not confined to any such principle because cast iron may be "modified" without losing either manganese or sulphur. It should be emphasized here that we are discussing the ranges of carbon, silicon, manganese and sulphur found in common gray foundry iron.

Assuming that the size of the graphite flakes in gray iron is governed by the stability of the carbide, it is still impossible to interpret this variation in stability in terms of the usual variations in manganese and sulphur. Some other factor must be considered.

Two general methods of approach have been made to this problem. The first involves the idea of supercooling of the melt due to the absence of certain inclusions which initiate freezing: Supercooling would naturally produce fine graphite like that shown at *A* in Fig. 52. The part shown at *B* contains normal flakes and therefore, if we credit this theory, did not supercool. It is difficult to understand how two such postulated conditions could exist side by side. "Modified" structures, produced by bubbling gases through molten cast iron, are generally characterized by irregular spots of fine graphite mixed with regions containing normal graphite flakes. That irregular spots should differ in composition seems more reasonable than that they should differ in supercooling. An idea based on composition calls for the presence of some material not shown by ordinary analysis, which is the second method of approaching the problem of "modification."

#### PREPARATION OF "OXYGEN-FREE" CAST IRON

Oxygen has been suggested as a possible cause of the irregular behavior of cast iron by many writers. Gillett<sup>1,10</sup> has abstracted much of the literature on this subject and the interested reader is referred to his bibliography. The effect of oxygen might be studied in the laboratory if a way could be found to remove it completely from the molten metal. "Deoxidation" in the usual steelmaking sense would not mean much where inclusions are a possible cause of abnormal behavior. Deoxidation by melting in an atmosphere of hydrogen is one way of approaching the problem.

The equipment at Battelle Memorial Institute includes a furnace built especially for melting steels under various gases of high purity. It consists essentially of a high-frequency induction furnace covered with a metal dome, fitted with observation windows and means for manipulating the crucible cover from the outside. Auxiliary apparatus is provided for the purification and storage of gases. Many low-carbon steels have been prepared in this furnace under an atmosphere of hydrogen on which vacuum-fusion analyses have been made at the University of Michigan. The oxygen percentages reported are in the fourth place of decimals.

A melt of synthetic cast iron was prepared in this furnace under hydrogen, using the technique developed in the melting of the steels. The charge was made up of disks of 20-gauge sheet steel which had been annealed in hydrogen for 72 hr. at 1900° F. This steel had the following analysis before fusion: C, 0.02 per cent; Mn, 0.13; P, 0.020; S, 0.040; O, 0.0089; N, 0.0088. It was placed in a clean magnesia crucible with a

quantity of graphite and melted down under hydrogen which had been carefully purified and dried. The resulting high-carbon alloy was held for one hour at 2850° F. At this stage an addition of silicon carbide was made by means of a tilting scoop manipulated from the outside. The idea here was to remove the oxygen from the iron-carbon alloy before the silicon went into it. Absorption of the silicon carbide was very rapid and the resulting alloy was held another hour under hydrogen at 2850° F., after which the power was cut off and the melt allowed to freeze in the crucible.

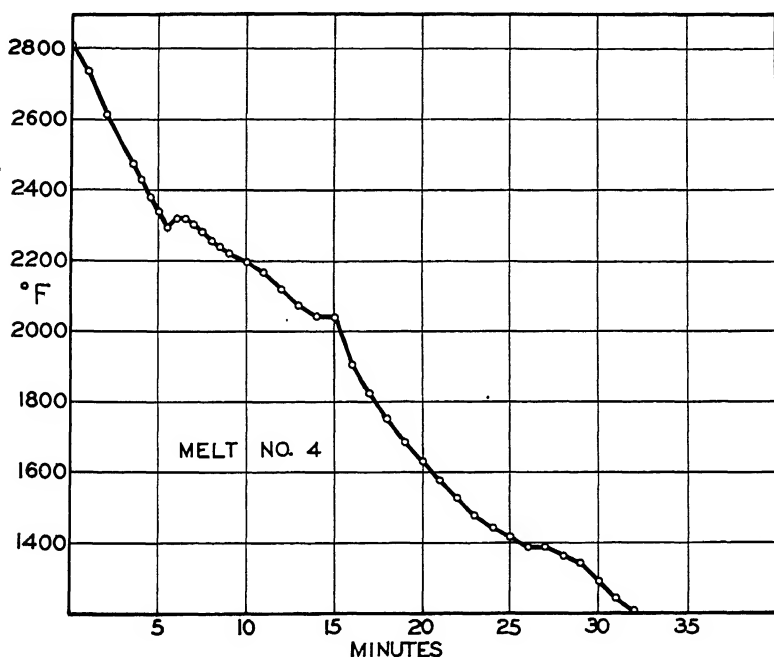
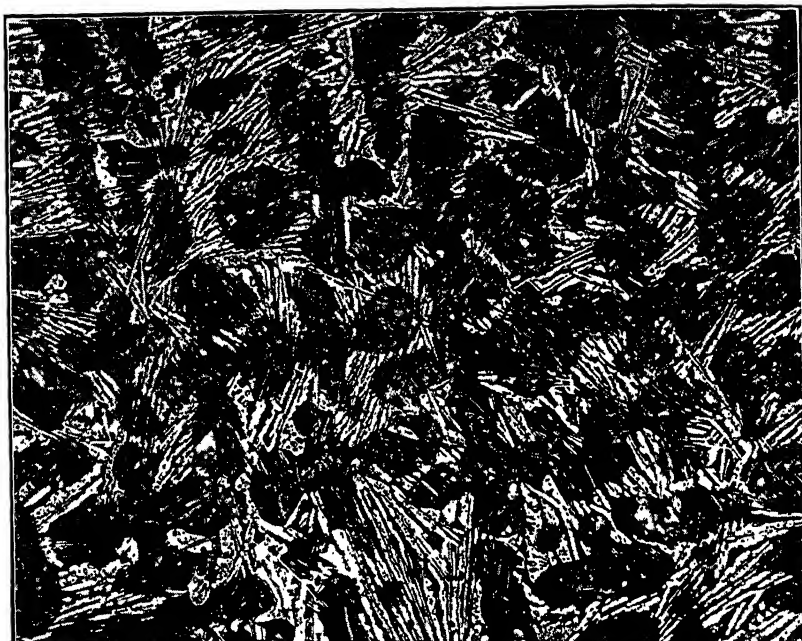


FIG. 53.—COOLING CURVE OF MELT NO. 4.

The maximum temperature reached by this melt was determined as follows. A platinum-platinum rhodium thermocouple in a silica protection tube was arranged so that it could be manipulated from the outside of the furnace through an airtight connection. During melting an optical pyrometer was sighted through a small hole in the graphite cover of the crucible. Soon after cooling started the thermocouple, which had been carefully preheated, was introduced into the molten metal and simultaneous readings were taken with thermocouple and optical pyrometer. The optical readings were favored by the fact that the top surface of the metal was perfectly clean. Over the temperature range from 2800° to 2200° F., the optical pyrometer read from 470° to 340° F. lower than the thermocouple. (This difference includes the error due to emissivity,

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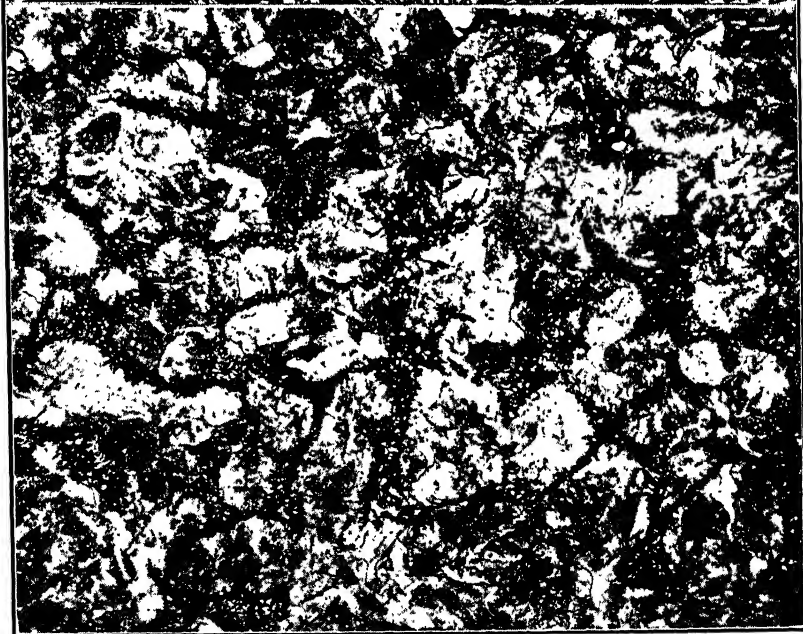


FIG. 54.—ALLOY NO. 4. MADE UNDER HYDROGEN. HELD ONE HOUR AT 2850° F. AND SLOW-COOLED. ETCHED IN  $\text{HNO}_3$ .  $\times 100$ .  
C, 2.70 per cent; Si, 1.67; S, 0.031; Mn, 0.08; P, 0.02.

FIG. 55.—SAME METAL AS IN FIG. 54. REMELTED IN HYDROGEN AND HELD 10 MINUTES AT 2500° F. ETCHED IN  $\text{HNO}_3$ .  $\times 100$ .

absorption by the furnace window and reflection from a Stellite mirror at 45° incidence.) By extrapolation of the curves plotted from the two sets of readings, the highest temperature reached was estimated at 2850° F. All the thermocouple readings are shown plotted in Fig. 53.

The resulting ingot of synthetic cast iron (alloy No. 4) was  $2\frac{1}{2}$  in. in diameter by 3 in. high and weighed about four pounds. It had the following analysis: T.C., 2.70; Si, 1.67; Mn, 0.08; S, 0.031; P, 0.020. The ingot was white all the way through and had the usual structure of white iron. Fig. 54 shows a typical spot consisting of pearlite and eutectic carbide. The outer surface of the melt for a depth of about  $\frac{1}{16}$  of an inch was graphitized and showed a structure like Fig. 55. In view of its composition and rate of cooling, the behavior of the alloy in freezing white is rather unusual. It is comparable in composition and rate of cooling to sample No. 46, which had the structure of a normal gray iron (Fig. 42). Something happened to the alloy made under hydrogen, which caused a great increase in the stability of its carbide.

From the standpoint of composition we might attribute the increased stability either to a loss in oxygen or a gain in hydrogen. The metal was superheated under hydrogen during the continuous stirring of induction melting, a thing that would favor both causes. A possible way of studying the question would be by remelting the white iron in vacuo. Vacuum fusion, in the presence of carbon, will remove oxygen from ferrous metals along with other gases present in them. Remelting the white iron in vacuo could hardly raise its oxygen content, but it would surely lower the amount of hydrogen present. If the carbide stability is due to a lack of oxygen the metal should remain white after vacuum fusion followed by cooling at the same rate employed in the hydrogen furnace. On the other hand, if hydrogen is a cause of carbide stability, vacuum fusion should promote graphitization by removing hydrogen.

All this is based on the assumption that the crucible material used is not reduced by the melt. The work of Reeve<sup>6</sup> on the fractional vacuum-fusion method of analysis has shown that the oxides of iron, manganese and silicon are reduced by carbon in vacuo at temperatures below 1300° C. (2370° F.). On a known sample the typical results are as given in Table 5.

A sample of cast iron melted and held in vacuo at a temperature of 2500° F. (1370° C.) should lose most of its oxygen present as FeO, MnO

TABLE 5.—*Reduction in Vacuo*

Oxide	Temperature of Reduction, Deg. C.	Yield of Oxygen as CO, Per Cent
Iron oxide.....	1000-1050	97.3
Manganous oxide.....	1150	86.9
Silica.....	1300	100.0
Alumina.....	1550-1600	75.0



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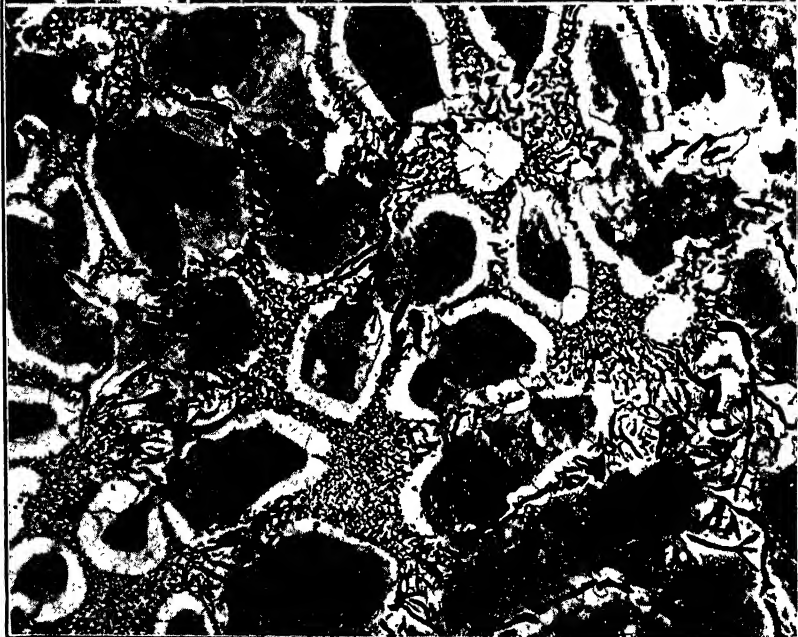


FIG. 56.—SAME METAL AS IN FIG. 54. REMELTED IN NITROGEN AND HELD 10 MINUTES AT 2500° F. ETCHED IN  $\text{HNO}_3$ .  $\times 100$ .

FIG. 57.—SAME METAL AS IN FIG. 54. REMELTED IN VACUO AND HELD ONE HOUR AT 2500° F. ETCHED IN  $\text{HNO}_3$ .  $\times 100$ .

and  $\text{SiO}_2$ . The crucible might conveniently be made of  $\text{Al}_2\text{O}_3$ , which is not reduced until  $2825^\circ \text{F.}$  ( $1550^\circ \text{C.}$ ) is reached. Reeve also found that hydrogen was given off in the fractions below  $2500^\circ \text{F.}$  On the basis of this work a number of vacuum melts were made on alloy No. 4.

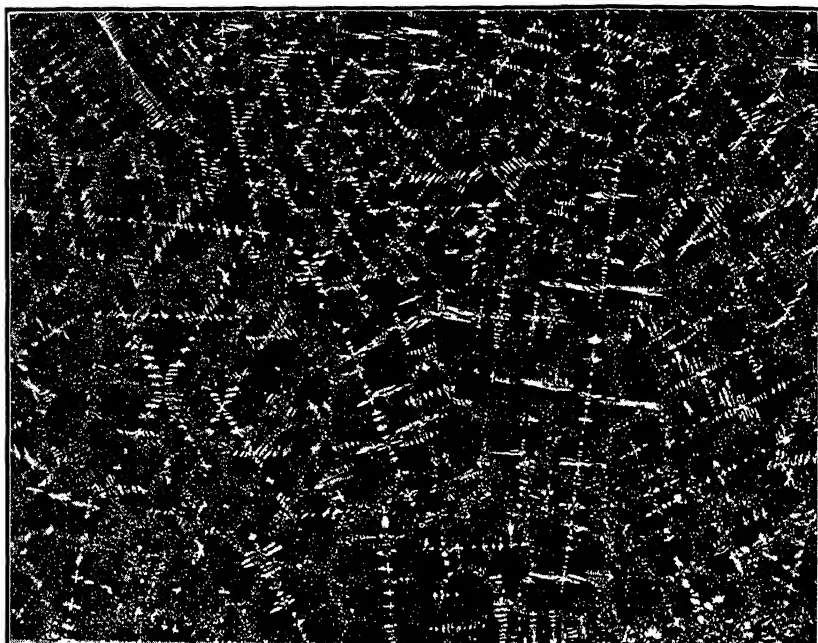
Pieces weighing 50 grams were melted in three types of crucibles: graphite, alundum and fire clay. The same Globar furnace was used in order that these melts might be comparable to previous work done at atmospheric pressure. By fitting water-cooled stoppers to the furnace tube, it was possible to hold the pressure well below 1 mm. of mercury at  $2500^\circ \text{F.}$  According to Vacher and Jordan<sup>7</sup>, a pressure of 2 mm. of mercury is sufficiently low to permit a reduction of the oxides. Pressures of this order will also remove hydrogen and nitrogen.

#### EFFECT OF VACUUM MELTING ON ALLOY NO. 4

Fig. 57 shows the structure produced by remelting the white iron in vacuo in an alundum crucible and holding one hour at  $2500^\circ \text{F.}$  It consists of pearlite and ferrite with much fine graphite and a few normal flakes. Brinell hardness has dropped from 415 to 140. The cooling rate over the range from  $2400^\circ$  to  $2000^\circ \text{F.}$  is comparable to that of the original melt. (Compare Fig. 17 with Fig. 53.) The difference in the structures shown in Figs. 54 and 57 must be an effect of vacuum melting alone. Melting the white iron in a clay crucible and holding in vacuo for 10 min. at  $2500^\circ$  produced a structure identical to Fig. 57. Melting in graphite and holding one hour at  $2500^\circ \text{F.}$  also had the same effect on the structure. This melt, of course, was saturated with carbon at  $2500^\circ \text{F.}$  and became hyper-eutectic. It contained, in the upper part of the melt, large flakes of "kish" which had floated to the top during cooling. The lower third was of eutectic composition and consisted of very fine particles of graphite in a matrix of ferrite and pearlite. The Brinell hardness of the eutectic portion was 160. All three melts gave evidence of a vigorous evolution of gas because small metal shot were found in the bottom of the furnace after each run.

Both vacuum fusion and melting in hydrogen are deoxidizing processes. It is hard to explain the change in structure of this alloy from the standpoint of oxygen content. From the conditions under which the alloy was made, it seems more likely that the element involved is hydrogen. The conclusion naturally follows that hydrogen is able to stabilize the carbide in cast iron. When considered in connection with the effect of carbide stability on the graphite flake size, such an idea offers interesting possibilities. There is no harm in following up a thing of this kind, provided we keep clearly in mind the fact that it rests upon limited circumstantial evidence. The work described below is concerned with the effects produced by melting cast iron under reduced pressure and remelting it in hydrogen gas. On the basis of such evidence an attempt is made to

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FIG. 58.—SAMPLE NO. 73. MELTED IN VACUO. BRINELL HARDNESS 120.  
FIG. 59.—SAMPLE NO. 77. MELTED IN AIR AT PRESSURE OF 100 MM. MERCURY.  
BRINELL HARDNESS 125.  
Both etched in  $\text{HNO}_3$ .  $\times 20$ .

interpret the structural changes in terms of the hydrogen content of the metal. Two basic assumptions are involved:

1. The size of the graphite flakes in cast iron is influenced by the stability of the eutectic carbide.

2. Hydrogen increases the stability of the carbide in cast iron.

The first idea has already been discussed in connection with the mechanism of freezing and the effect of sulphur on alloys of iron, carbon and silicon. The second idea is suggested by the behavior of alloy No. 4, which froze white after superheating under hydrogen.

#### EFFECT OF VACUUM MELTING ON NORMAL CAST IRON

A cast iron of the following analysis (iron No. 228) was selected: C, 3.70 per cent; Si, 2.24; S, 0.028; Mn, 0.68; P, 0.157.

Samples weighing 50 grams were melted and slow-cooled in the Globar furnace, using the standard heating and cooling cycle.

*Sample No. 73.* Melted in a clay crucible in vacuo. Held 10 min. at 2500° F. Fig. 58 shows the resulting structure. The graphite is so fine that individual particles are not visible at this magnification. The matrix is ferrite with some scattered patches of pearlite. Melting in graphite and in alundum and holding one hour in vacuo at 2500° F. gave structures exactly like Fig. 58.

*Sample No. 77.* Melted in a clay crucible in air at a pressure of 100 mm. of mercury. Held 10 min. at 2500° F. There is a marked increase in the size of the graphite flakes (Fig. 59). The matrix is the same as in Fig. 58.

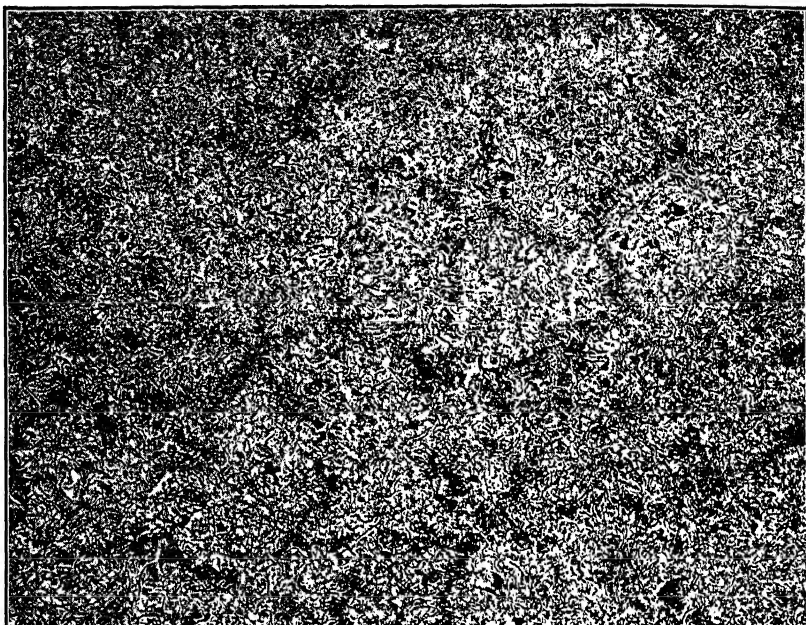
*Sample No. 78.* Melted in a clay crucible in air at a pressure of 200 mm. of mercury. Held 10 min. at 2500° F. The graphite flakes have increased still more in size. (Compare Fig. 60 with Fig. 59.) Pearlite occurs in the boundaries of the cell structure.

*Sample No. 79.* Melted in a clay crucible in air at a pressure of 400 mm. of mercury. Held 10 min. at 2500° F. Both the size of the graphite flakes and the amount of pearlite have increased (Fig. 61).

*Sample No. 74.* Melted in a clay crucible in air at atmospheric pressure. Held 10 min. at 2500° F. The size of the flakes has increased still more (Fig. 62). The matrix is ferrite and pearlite.

The gradual change in structure exhibited in this series of melts may reasonably be attributed to the gradual removal of some gas from the molten metal. Three gaseous elements are usually present in ordinary cast iron: oxygen, nitrogen and hydrogen. Changes produced by melting at reduced pressure may be due to a loss of one or more of these elements. Remelting samples of the modified metal in each of these gases would test the reversibility of the change and throw some light on the matter. The first gas tried was hydrogen.

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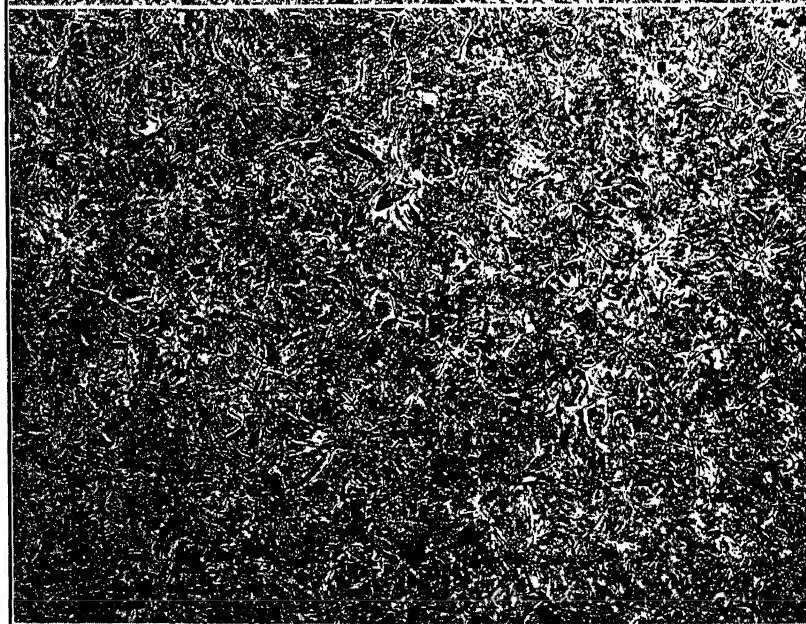


FIG. 60.—SAMPLE No. 78. MELTED IN AIR AT PRESSURE OF 200 MM. MERCURY.  
BRINELL HARDNESS 127.

FIG. 61.—SAMPLE No. 79. MELTED IN AIR AT PRESSURE OF 400 MM. MERCURY.  
BRINELL HARDNESS 132.

Both etched in  $\text{HNO}_3$ .  $\times 20$ .

A number of modified samples were prepared by melting the normal cast iron (No. 228) in vacuo. These same pieces were remelted in hydrogen which had been carefully purified and dried. The Globar furnace was used and the standard heating and cooling cycle was maintained. Alundum crucibles were used for all the melts under hydrogen.

*Sample No. 87.* Melted in vacuo and held 10 min. at 2500° F. (The resulting structure was identical to Fig. 58.) Remelted in hydrogen and held one hour at 2200° F. Melting in hydrogen has produced an

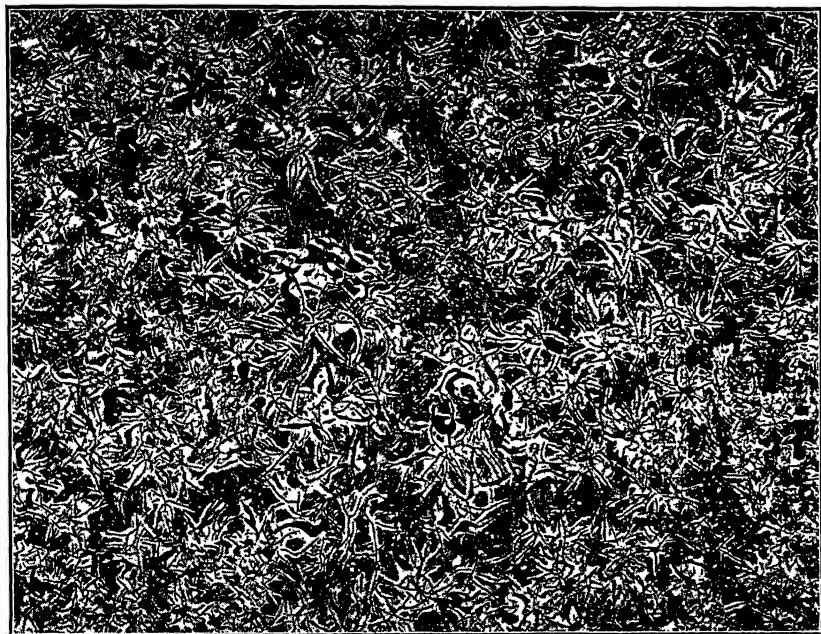


FIG. 62.—SAMPLE No. 74. MELTED IN AIR AT ATMOSPHERIC PRESSURE. ETCHED IN  $\text{HNO}_3$ .  $\times 20$ . BRINELL HARDNESS 107.

enormous increase in the size of the graphite flakes. (Compare Fig. 63 with Fig. 58.) They are larger than those in Fig. 62 and the amount of pearlite has also increased.

*Sample No. 88.* Melted in vacuo and held 10 min. at 2500° F. (The resulting structure was identical to Fig. 58.) Remelted in hydrogen and held one hour at 2300° F. Fig. 64 shows the result, which resembles Fig. 63 except that the graphite flakes are still larger.

*Sample No. 89.* Melted in vacuo and held 10 min. at 2500° F. (The resulting structure was identical to Fig. 58.) Remelted in hydrogen and held one hour at 2400° F. The amount of pearlite has increased but the graphite flakes are smaller than those in sample No. 88. (Compare Fig. 65 with Fig. 64.)

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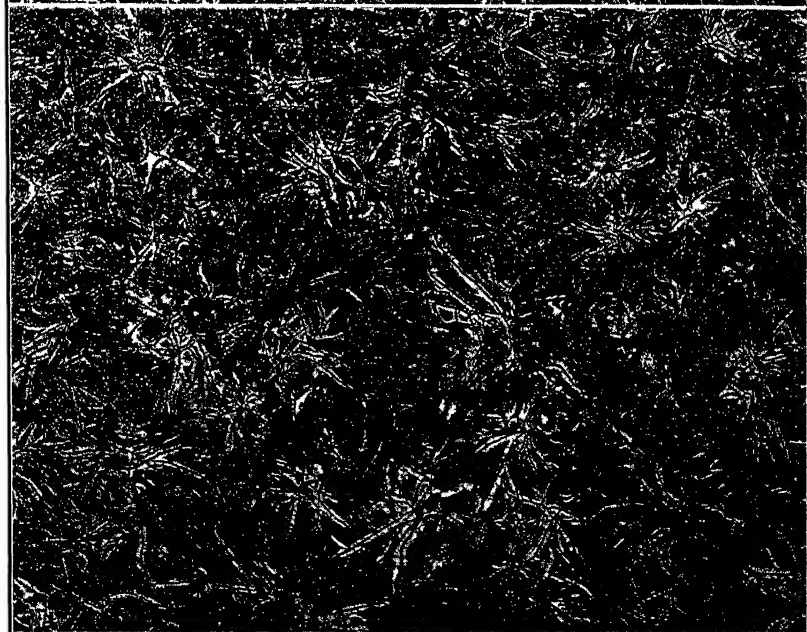
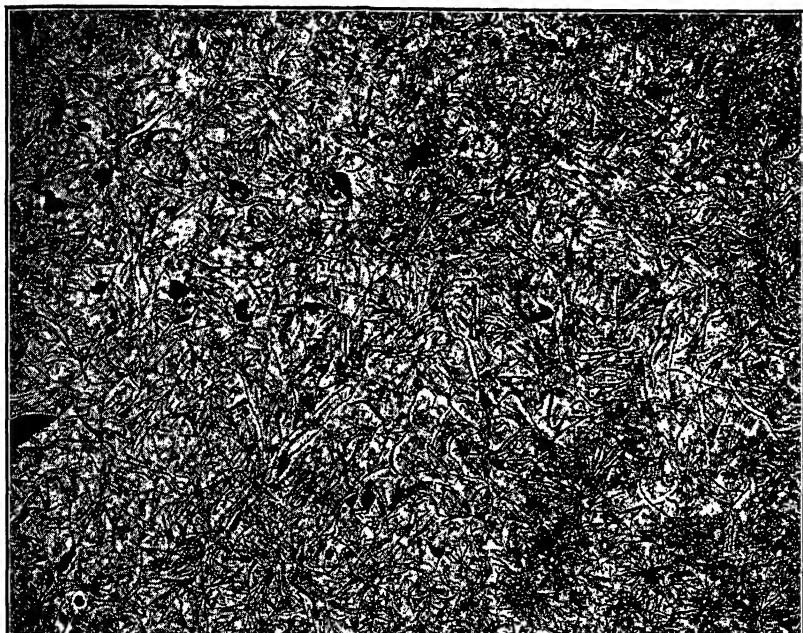


FIG. 63.—SAMPLE NO. 87. MELTED IN HYDROGEN AND HELD ONE HOUR AT 2200° F.  
BRINELL HARDNESS 96.

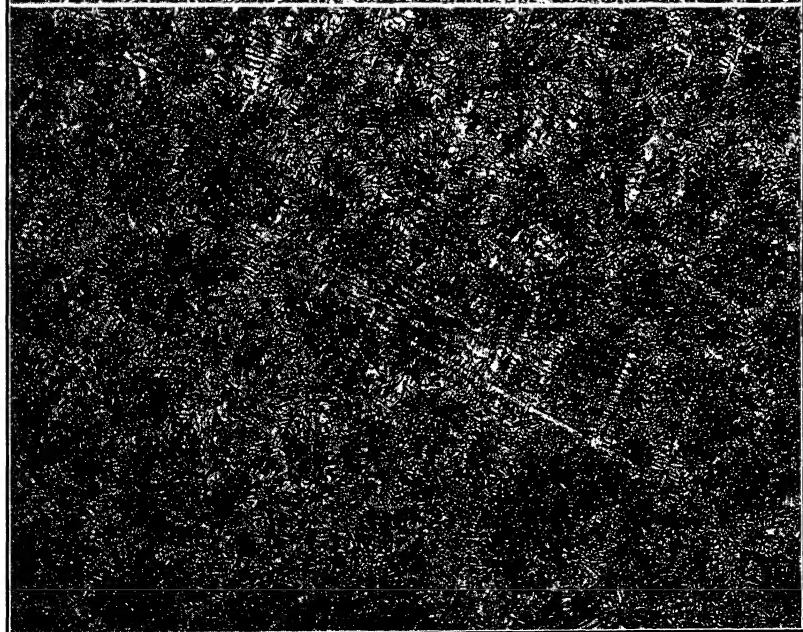
FIG. 64.—SAMPLE NO. 88. MELTED IN HYDROGEN AND HELD ONE HOUR AT 2300° F.  
BRINELL HARDNESS 98.

Both etched in  $\text{HNO}_3$ .  $\times 20$ .





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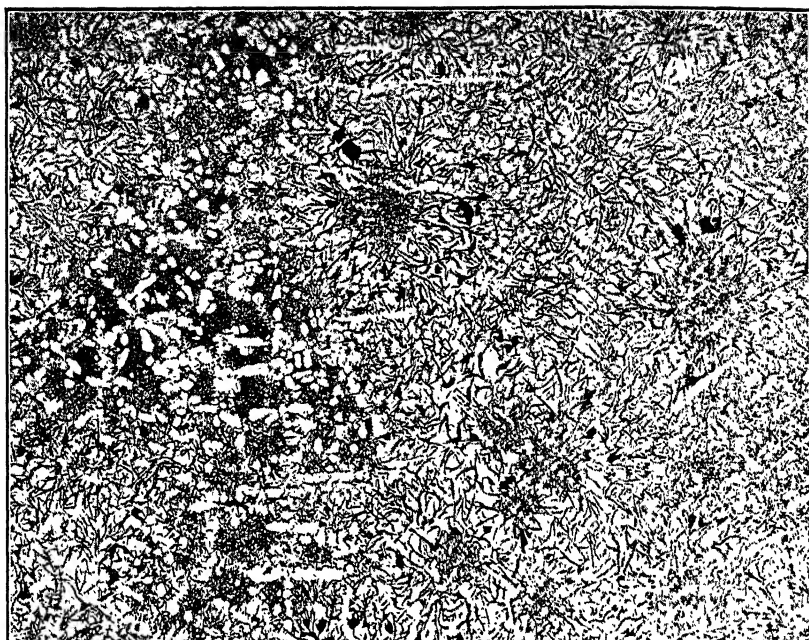
FIG. 65.—SAMPLE No. 89. MELTED IN HYDROGEN AND HELD ONE HOUR AT 2400° F.  
BRINELL HARDNESS 130.

FIG. 66.—SAMPLE No. 82. MELTED IN HYDROGEN AND HELD ONE HOUR AT 2500° F.  
BRINELL HARDNESS 137.

Both etched in  $\text{HNO}_3$ .  $\times 20$ .



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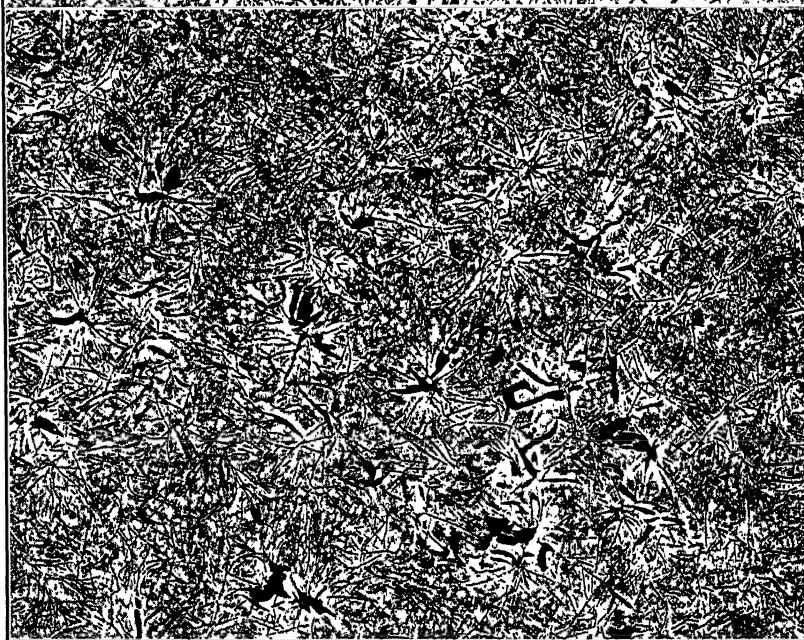


FIG. 67.—SAME METAL AS IN FIG. 64 REMELTED IN VACUO.  
FIG. 68.—SAME METAL AS IN FIG. 67 REMELTED IN HYDROGEN AND HELD ONE HOUR AT  
2300° F.  
Both etched in  $\text{HNO}_3$ .  $\times 20$ .

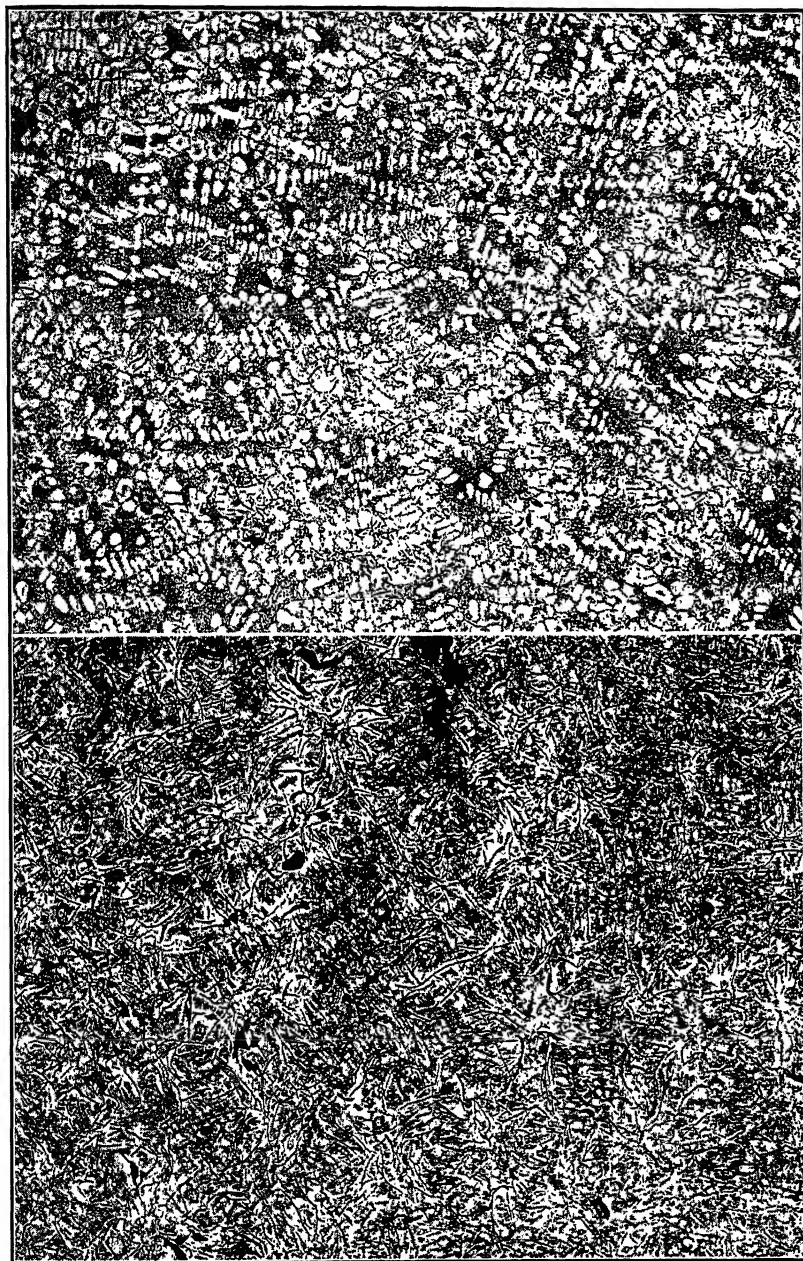


FIG. 69.—SAME METAL AS IN FIG. 68 REMELTED IN VACUO.

FIG. 70.—SAME METAL SHOWN IN FIG. 69 REMELTED IN HYDROGEN AND HELD ONE HOUR AT 2300° F.

Final analysis: C, 3.09 per cent; Si, 2.16; S, 0.014; Mn, 0.04.

Both Figs. 69 and 70, etched in  $\text{HNO}_3$ .  $\times 20$ .

*Sample No. 82.* Melted in vacuo and held 10 min. at 2500° F. (The resulting structure was identical to Fig. 58.) Remelted in hydrogen and held one hour at 2500° F. Fig. 66 shows the resulting structure. The size of the graphite flakes has decreased greatly. (Compare with Fig. 65.) Only a few traces of ferrite occur in the matrix.

In order to check the reversibility of the change produced by vacuum melting and melting in hydrogen, the following experiment was carried out. The same metal shown in Fig. 64 was remelted in vacuo and held one hour at 2500° F. in an alundum crucible, with the result shown in Fig. 67. Carbon has been lost in melting and primary dendrites are now becoming prominent. The matrix is ferrite containing fine graphite and rosettes of graphite flakes.

The same piece of metal was again remelted in hydrogen and held one hour at 2300° F., with the result shown in Fig. 68. A complete restoration has taken place. (Compare Fig. 68 with Fig. 64.)

The same metal was remelted in vacuo and held one hour at 2500° F. Fig. 69 shows the resulting structure. More carbon has been lost and consequently more primary dendrites have formed. The matrix is ferrite containing very fine graphite.

The same metal was finally remelted in hydrogen and held one hour at 2300° F., with the result shown in Fig. 70. A reversion to the original structure has taken place. Notice how the primary dendrites have restricted the growth of the graphite flakes in Fig. 70.

Apparently this reversal of structure could be repeated as often as desired. There is, of course, a change in analysis caused by the repeated meltings but a complete reversal of structure cannot be attributed to any such gradual change in composition. It seems more likely that the effect is due to the introduction and removal of hydrogen.

The structure shown in Fig. 58 is identical to the part marked *A* in Fig. 52. It will be recalled that this modified cast iron reverted to normal on remelting. The portion *B* in Fig. 52 is identical to Fig. 62, a normal cast iron. If the metal shown in Fig. 58 is remelted in air or in commercial nitrogen, it becomes exactly like Fig. 62. This was checked on numerous samples. It has just been shown that melting in pure hydrogen produces the same effect. The question arises as to whether air or nitrogen would be able to produce this change if no hydrogen were available in the furnace atmosphere. Samples of the normal cast iron (No. 228) which had been modified by vacuum fusion were remelted in air, which had been dried, and in purified nitrogen. It was found that the extent to which the modified structure was retained depended on the care taken in drying the gases. The graphite flake size in the various melts ranged from that shown in Fig. 59 to that in Fig. 61. Graphite of the finest size was obtained with the following procedure.

*Sample No. 109.* A volume of air was stored in contact with magnesium perchlorate for about 15 hr. The melt was brought up to 2400° F. under vacuum with continuous pumping. At this temperature the dry air was let in and the furnace was heated to 2500° F., held 10 min. and slowly cooled as usual. The resulting structure is shown in Fig. 71. The graphite is not as fine as that produced by vacuum melting but it is decidedly modified (compare with Fig. 58).

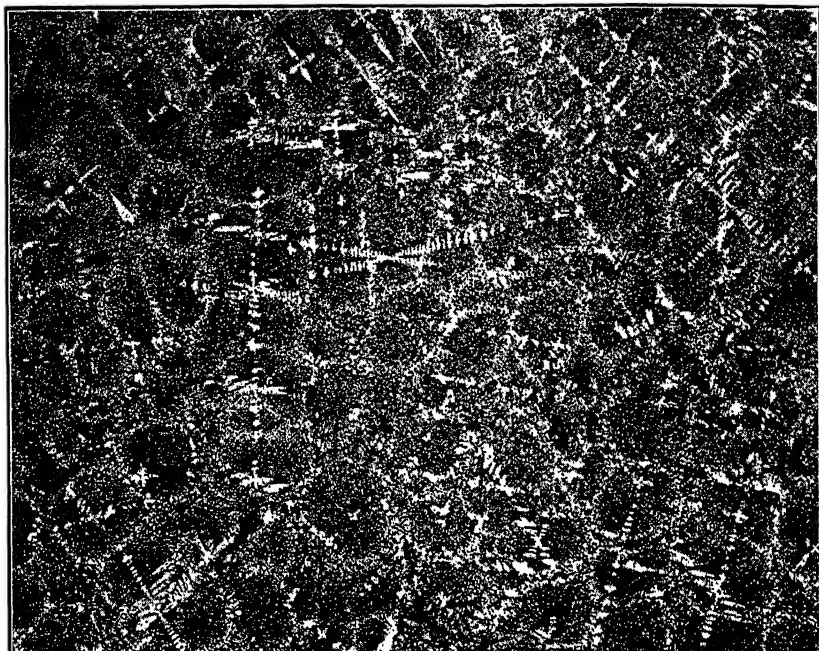
*Sample No. 108.* The procedure described above was repeated with nitrogen from the same tank used in all previous work. The gas was purified by bubbling through sulphuric acid, passing over copper turnings held at 1600° F. and finally through calcium chloride and magnesium perchlorate. It was then stored in contact with the drying agent for about 24 hr. Fig. 72 shows the structure obtained by melting in the purified gas.

The results indicate that the changes produced by melting modified cast iron in air and in nitrogen are due to the absorption of hydrogen from water vapor in the furnace atmosphere. They also indicate that neither nitrogen nor oxygen is able to produce a change in the size of the graphite flakes. It is thus possible to interpret the series of structures shown from Figs. 58 to 66 in terms of hydrogen content.

The solubility of hydrogen in pure iron increases with increasing temperature. Bardenheuer<sup>8</sup> claims the same thing is true for cast iron. On this assumption a series of melts made under hydrogen at increasing temperatures should contain increasing amounts of the gas. The same cast iron melted under reduced pressure should contain an amount of hydrogen which decreases as the pressure becomes lower. Thus we may form a continuous series of hydrogen contents varying from the lowest, shown in Fig. 58, to the highest, shown in Fig. 66. The effect on the graphite flakes is at once seen to be similar to that of sulphur on the iron-carbon-silicon alloys. The flakes increase in size with increasing hydrogen content up to a maximum, after which they become smaller again. Such an effect is in agreement with the postulate that hydrogen increases the stability of the carbide in cast iron.

It will be recalled that the alloys of iron, carbon and silicon differed from modified cast iron in that they were not changed by melting in nitrogen or in air. The response of these alloys to vacuum melting and melting in hydrogen was therefore determined. Fig. 73 shows alloy No. 8 melted in vacuo in an alundum crucible and held one hour at 2500° F. There is no change in the structure (compare Fig. 73 with Fig. 29). Remelting in hydrogen gave the result shown in Fig. 74, which is a very odd type of structure. The rosettes in this specimen are about  $\frac{1}{4}$  in. in actual diameter and only a part of one can be shown in the photograph. A marks the center at which freezing started and the cell boundary is located near B. (This was determined by heat-tinting.) The

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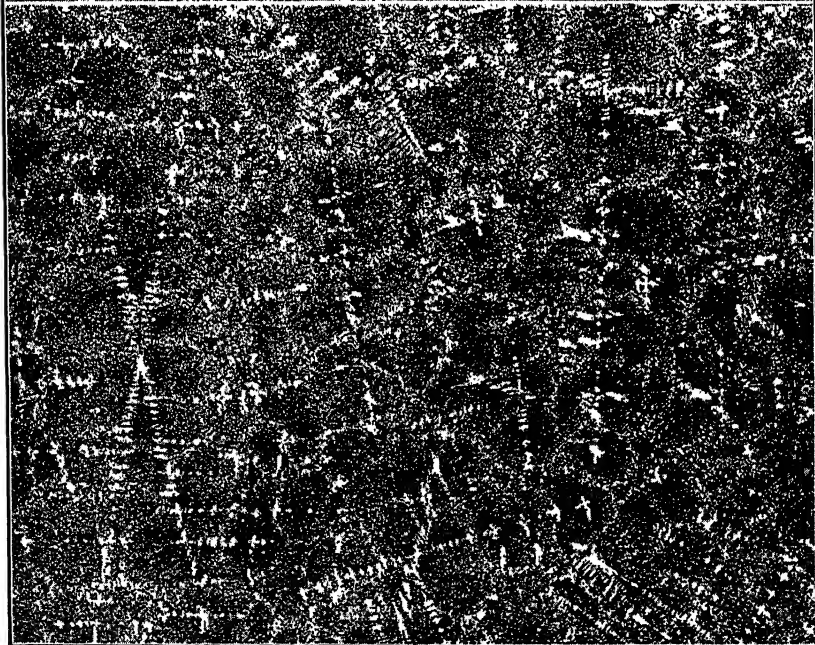
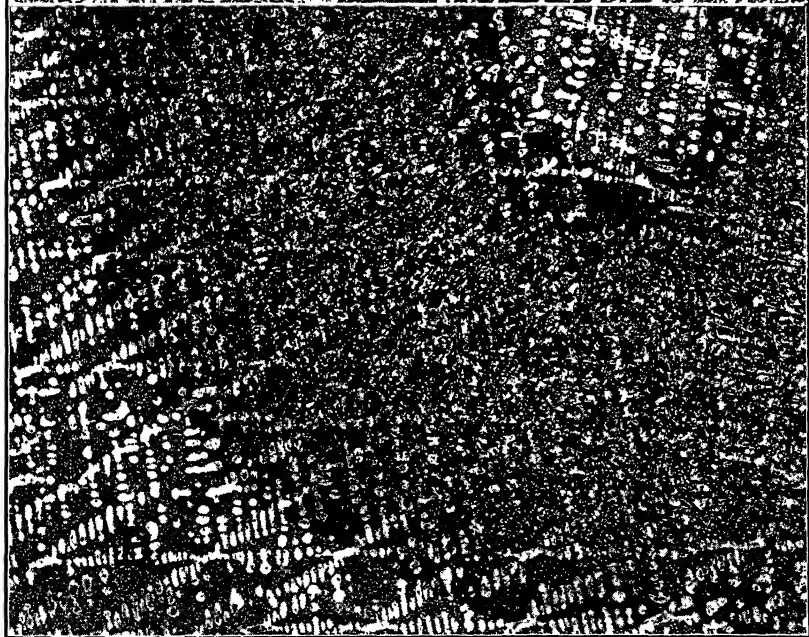


FIG. 71.—SAMPLE NO. 109. MODIFIED CAST IRON REMELTED IN DRY AIR.  
FIG. 72.—SAMPLE NO. 108. MODIFIED CAST IRON REMELTED IN DRY NITROGEN.  
Both etched in  $\text{HNO}_3$ .  $\times 20$ .





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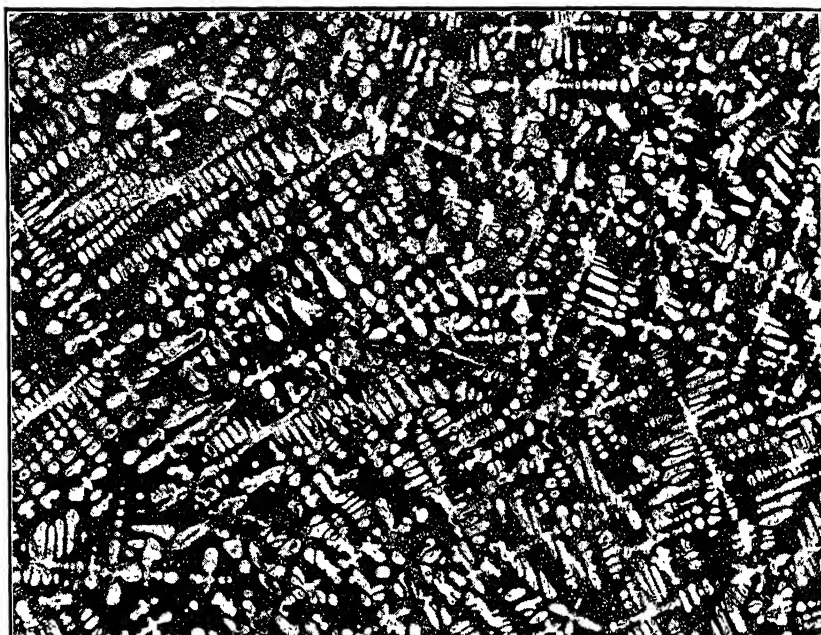
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FIG. 73.—ALLOY NO. 8 MELTED IN VACUO.

FIG. 74.—SAME METAL AS IN FIG. 73 REMELTED IN HYDROGEN AND HELD ONE HOUR AT 2500° F.

Both etched in  $\text{HNO}_3$ .  $\times 20$ .

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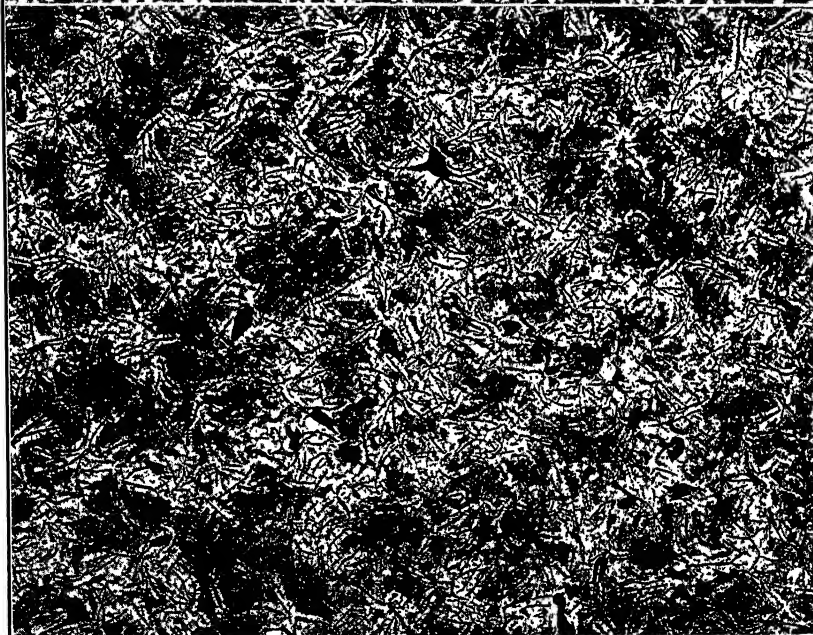


FIG. 75.—ALLOY NO. 8 PLUS 0.09 PER CENT MN AND 0.032 PER CENT S MELTED .  
VACUO.

FIG. 76.—SAME METAL AS IN FIG. 75 REMELTED IN HYDROGEN AND HELD ONE HOUR .  
2300° F.

Both etched in  $\text{HNO}_3$ .  $\times 20$ .

portion around *A* is ferrite and fine graphite. Between *A* and *B* a ring of pearlite occurs in which graphite flakes are arranged in the form of a huge rosette. The cell boundary near *B* is again ferrite and fine graphite. It should be noted that the flakes in the huge rosette are no larger than those in the small rosettes of Fig. 73.

A striking similarity exists between Fig. 67 and Fig. 73. The modified cast iron closely resembles the iron-carbon-silicon alloy. Melting in hydrogen, however, produces entirely different results in the two cases as may be seen by comparing Fig. 68 with Fig. 74. The iron-carbon-silicon alloys do not respond to hydrogen in the same way as cast iron. It was found that this difference is due to the presence of manganese and sulphur, as illustrated by the following case.

*Sample No. 98.* Alloy No. 8 plus 0.09 per cent Mn and 0.032 per cent S. Fig. 75 shows the result of melting in vacuo and holding one hour at 2500° F. The matrix is ferrite with a few traces of pearlite. All the graphite is extremely fine. Fig. 76 is the same alloy remelted in hydrogen and held one hour at 2300° F. The result is a normal cast-iron structure consisting of large graphite flakes in a matrix of ferrite and pearlite. (Compare Fig. 76 with Fig. 68.) The addition of manganese and sulphur has caused the iron-carbon-silicon alloy to respond to hydrogen in the same manner as cast iron. A comparison of Fig. 74 with Fig. 76 will illustrate the change produced by the addition of these elements. A systematic study of the effect of manganese, sulphur and hydrogen on alloys of iron, carbon and silicon is under way at present. All the melts examined so far have shown the same response as the one reported here. The effect varies with varying manganese and sulphur but sufficient data have not been collected to permit generalization.

#### INFLUENCE OF HYDROGEN ON CAST IRON

On the basis of the experiments described above a hypothesis is proposed to explain the phenomenon of modification in cast iron. Three factors may be borne in mind:

1. That cast iron is essentially an alloy of iron, carbon and silicon whose structure is profoundly altered by the presence of manganese, sulphur and hydrogen.

2. That the type of structure called "normal" is due to the influence of the last three elements.

3. That by varying the amounts of manganese, sulphur and hydrogen, a great variety of structures can be produced with the same rate of cooling.

To illustrate the effect of varying the hydrogen content the following examples are pointed out. Fig. 54 shows an alloy that froze white because it was saturated with hydrogen at 2850° F. This is a case of extreme carbide stability. Fig. 55 shows the same metal remelted in hydrogen at 2500° F. The hydrogen content has dropped sufficiently to permit



graphitization and fine graphite has resulted from very slow carbide dissociation. Fig. 56 shows the same white iron remelted in nitrogen at 2500° F. The hydrogen content is still lower and the rate of graphitization favored the formation of normal flakes. Fig. 57 is the same alloy melted in vacuo at 2500° F. Much hydrogen has been lost and fine graphite flakes were formed by rapid carbide dissociation. All these melts were cooled at substantially the same rate.

The point to be emphasized here is that fine graphite may originate at both ends of the range, either by very slow or by very rapid graphitization. In considering the effects of hydrogen the influence of other elements must of course be kept in mind. Raising the silicon in Fig. 54 would doubtless have promoted graphitization. Lowering the sulphur would act likewise. Raising the manganese would influence the sulphur. Raising the carbon would influence the whole mechanism of freezing and segregation, with consequent effects on graphitization. Cast iron is a very complex alloy and it is doubtful whether its behavior is subject to interpretation in terms of any single factor, chemical or physical. The hydrogen hypothesis simply recognizes this element as one factor influencing the behavior.

By recognizing a gas as one of the basic constituents, we offer an immediate explanation for the response of cast iron to various furnace atmospheres. Assuming that the solubility of this gas is a function of temperature, many of the effects of superheating may be interpreted. (Fig. 55 resembles a low-carbon cast iron with too much superheating.) Assuming further that some of the hydrogen may be removed from the molten metal by bubbling or mechanical agitation, still another class of phenomena may be explained. Norbury's process of blowing carbon dioxide through the metal simply sweeps out some of the hydrogen normally present and produces the same effect as melting under reduced pressure. Blowing hydrogen through the modified metal restores the original condition, as is stated by Norbury<sup>9</sup>. The fact that this process works best on small ladles of metal is in line with such an explanation.

No attempt is made here to explain how hydrogen causes an increase in carbide stability. In this study, the phenomenon of modification has been approached from the standpoint of composition only. The basic problem was that of determining what elements really constitute cast iron. A complete analysis of everything present would not solve this problem because we still have the question of deciding what is essential. The most direct method is synthetic. Starting with a base alloy of iron, carbon and silicon, it is required to find what elements are absolutely necessary to reproduce completely the structure and properties of cast iron. This is a very complex problem and the experiments reported above can hardly be considered a first approximation. In conclusion, it is emphasized that the postulated action of hydrogen rests upon very

limited circumstantial evidence. The hypothesis is offered simply as a possible explanation of why the graphite flakes in cast iron vary so widely without apparent cause. Any study of the mechanism of freezing must involve a consideration of this problem.

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## DISCUSSION

(James T. MacKenzie presiding)

B. C. BURGESS,\* Spruce Pine, N. C.—Has the coarseness or fineness of the phosphite network any connection with the course taken or the grain size of the cast iron?

A. BOYLES.—As to the coarseness of the network—what I call the cell structure—I could not find anything systematic in that. For example, the dendrites are always the same size with the same rate of cooling, but the cells seem to vary widely. I do not think there is any relationship between the cells and austenitic grain size, using that term as it is applied to steel. This cell structure originates in the freezing and seems to be a result of selective solidification.

R. M. ALLEN,† Bloomfield, N. J.—Did you find in your studies at higher magnifications that the graphite precipitated out of the dendrites? In practically all of my work—of course, I did nothing in chilling from the liquid state but chilling from as near the temperature of solidification as possible—I have never found that the graphite precipitated out anywhere else but in the dendrites. That is one question.

Fig. 77 is one of the primary dendrites, with secondary dendritic structure, and the graphite is present, within the dendrites.

Did you notice any unusual constituents such as occur in Fig. 78 in the ledeburite structure, which, of course, is breaking down to a pearlite? Is there a decided difference between the material enclosed within the dendrite? This is really a part of the dendrite. I think that the solution of many of our problems lies in a study of what is actually present in these constituents.

Have you ever noticed, in the primary precipitation of the graphite within the pearlitic structure, whether it was coming out in such extremely fine grains as are seen

\* Manager, Tennessee Mineral Products Corporation.

† Consulting Metallurgist.

in Fig. 79? That, of course, is a very high magnification, and to my way of thinking it represents one of the earliest evidences of the precipitation of graphite.

Is the ledeburite structure that is seen almost to perfection in Fig. 80, between the primary dendrites, fairly typical, or have you frequently found that that ledeburite



FIG. 77.—GRAPHITE PRECIPITATION IN PRIMARY DENDRITE.

FIG. 78.—DETAIL STRUCTURE OF LEDEBURITE.

FIG. 79.—EARLY STAGE OF GRAPHITE PRECIPITATION.

FIG. 80.—LEDEBURITE EUTECTIC IN CHILLED IRON.

Original magnifications as follows: Fig. 77,  $\times 1750$ ; Fig. 78,  $\times 2000$ ; Fig. 79,  $\times 2000$ ; Fig. 80,  $\times 200$ ; reduced  $\frac{1}{4}$  in reproduction.

structure was suppressed for one reason or another? That has been a question that has been of considerable interest to me because I have found instances where the ledeburite structure was completely suppressed, and other cases where it is developed as in this picture.

Have you studied the nature of the graphite flakes themselves? Fig. 81 shows a single graphite flake at a very high magnification, nearly 5000, showing, in my estima-

tion, that the graphite is made up of many small, more or less irregularly placed flakes, and that apparently they float into the larger flake and are amalgamated without losing their identity. It would be interesting to know whether that is actually the case when the irons are frozen from the liquid state.

A. BOYLES.—The specimens were studied at high magnification, mainly with a view to finding the effect of inclusions and that sort of thing. As nearly as I could tell the flakes are confined to the fillings of the primary dendrites. That was in alloys of about 2 per cent silicon.



FIG. 81.—SINGLE GRAPHITE FLAKE IN GRAY IRON.  
Original magnification 4500; reduced  $\frac{1}{4}$  in reproduction.

I have not studied white irons, and I do not believe you can compare white iron with a gray iron that has been quenched from the liquid state, either with regard to graphite or the structure of the carbide.

J. T. MACKENZIE,\* Birmingham, Ala.—The dendrites that you speak of, I take it, are not the dendrites Mr. Allen speaks of.

A. BOYLES.—Not necessarily.

R. H. SWEETSER,† New York, N. Y.—Are you sure that the crystal in Fig. 81 was entirely carbon? Was it 100 per cent carbon?

R. M. ALLEN.—As far as I know, it was.

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\* Metallurgist and Chief Chemist, American Cast Iron Pipe Co.

† Consulting Engineer.

R. H. SWEETSER.—Because we had some large graphite crystals that we caught as kish, and we were surprised to find that instead of being all graphite they had about 12 per cent silicon, so that we could not use the kish as a lubricant.\*

J. T. MACKENZIE.—Was any other substance present?

R. H. SWEETSER.—That is all that we determined, the carbon and the silicon.

MEMBER.—Was it silica or silicon?

R. H. SWEETSER.—Silicon.

H. A. SCHWARTZ,† Cleveland, Ohio (written discussion).—Starting with an admission of a “hereditary” characteristic in regard to graphite form in cast iron, Boyles has evolved a new and ingenious explanation for the formation of rosettes of graphite and a demonstration that the vagaries of carbide stability required in that explanation in order to explain changes in graphite morphology may be associated with the presence of hydrogen in cast iron. There seems to be no well organized attempt to show any “heredity” of hydrogen content under melting conditions as diverse as may be possible while still preserving the “heredity” with regard to graphite characteristics.

The author has modestly and wisely disclaimed any thought that his work forms a complete elucidation of the problem. This commentator suggests that logically the next step for Boyles or others who may wish to pursue the train of thought set up in the paper is a correlation of hydrogen content with melting stock and melting methods. Direct combustion methods for hydrogen in cast iron should place such an investigation within the scope of a laboratory interested in the subject.

Many previously unrelated facts come to one's mind which may well be explained by the hydrogen theory. This creates encouragement for exploring the ideas of the paper most fully and sympathetically. The apparently rather convincing demonstration that graphite “nuclei,” whatever they may prove to be, come out in the eutectic filler material and that all graphite formation occurs during the process of eutectic freezing, is most stimulating. The latter feature was explored by Coppersmith,<sup>11</sup> in the writer's laboratory, a year ago with results entirely in harmony with Boyles' more rigorous experiments.

The explanation of rosettes of graphite, the “kekume structure” of the Japanese investigators, in terms of freezing rate and graphitizing rate is novel, ingenious and extremely interesting. It suggests to future experimenters that experiments should be planned mainly in the very slightly hypoeutectic regions. Since the hyper-eutectic alloys must begin to crystallize as cementite or graphite, apparently often the latter, it seems entirely plain that the results on such alloys can not be comparable with the results on hypoeutectic metal or with Boyles' conceptions of the freezing process.

A separation of the phenomena of the rate of formation of crystallization centers for graphite and their rate of growth, which together make up the “eagerness” of metal to graphitize, would seem highly important.

One has not time in the interval between the preprinting and presentation of this paper to reflect upon all the implications of the author's hypothesis. Some difficulties suggest themselves which may be capable of explanation on more detailed study. Boyles explains the limitation of length of an individual graphite flake by a “pinching

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\* A sample of kish from a 150-ton mixer-type hot-metal ladle (March 1929) was found to contain—29.27 per cent carbon; 10.31 per cent silicon; 45.70 per cent iron; 1.22 per cent manganese; 13.50 per cent undetermined.

† Manager of Research, National Malleable and Steel Castings Co.

<sup>11</sup> Schwartz: Graphitization during Freezing of Cast Iron. *Min. and Met.* (Sept. 1936) 449.

off" process due to freezing becoming more rapid than graphite crystallization. How does this happen? Evidently since the flakes originally grew there was in the beginning a condition in which the graphite flakes grew radially at least as rapidly as the "austenitic(?)" sphere. If then there comes a time when the latter grows the faster, either the linear coefficient of crystal growth of graphite must have been retarded or the rate of freezing as measured by increase in radius must have been accelerated. Assuming that during eutectic freezing the iron, being at constant temperature, loses heat to a constant environment at constant rate, the amount of material solidifying per unit time should be constant and since the interface between solid and liquid constantly increases, the radial rate of growth of the spheroid should decrease, yet the hypothesis requires it to increase.

Does the relative area of graphite and solid solution at the interface play a part? Since graphite crystallizes in plates of roughly constant thickness, there will come a time when the areas of solid solution on the sphere's surface are larger in proportion to the areas of graphite than will permit the sphere to grow by deposition of equal thicknesses of graphite and "austenite(?)." New nuclei of graphite must then form or the graphite flake must grow outward beyond the solidified sphere or else perhaps the metastable eutectic may form. Evidently these are complexities to consider.

Boyles' work plainly bears directly on "mottled" cast irons. It is a matter of common shop observation that irons that at proper pouring temperatures produce a graphite-free fracture will, when poured cold, have very fine mottles, whereas those that are mottled, because of silicon and carbon content, even at normal pouring temperatures have much larger mottles. It is usually thought that the size of such mottles increases and their number decreases with temperature and that at high temperature the phenomenon of "inverse chill" is encountered.

One might go on correlating many observations with the ideas of the present paper but enough has probably now been said to indicate how thought provoking it is. The number of trains of ideas it suggests is probably the best proof of the value of the work reported.

A. BOYLES (written discussion).—The comments of Dr. Schwartz, who has done so much work on graphitization, are especially welcome. His discussion of the complexities involved in the formation of the rosettes omits one factor which, in the writer's opinion, is very important; i.e., the fact that the freezing is selective and that the composition of the liquid along the solid-liquid interface is constantly changing. Such segregation is known to occur in phosphorus and sulphur, and it is likely that hydrogen, whose solubility decreases abruptly at the freezing point, is also involved. The rate of graphitization may vary with the change in composition. Some method of detecting the segregation of silicon would be of great value in this connection.

## Oxides in Basic Pig Iron and in Basic Open-hearth Steel

By T. L. JOSEPH,\* MEMBER A.I.M.E.

(New York Meeting, February, 1937)

THE extent to which hot metal from the blast furnace affects open-hearth practice and the quality of steel produced has been discussed widely. Open-hearth operators have attributed difficulties experienced in making satisfactory steel to characteristics of the pig iron not disclosed by ordinary analysis. The commonest criticism of the iron has been that it is "physically cold" or "dirty." Often when the blast furnaces are working irregularly the quality of the iron is questioned. A cold hearth, slipping and hanging, the use in the past of unsintered flue dust, and the use of ores difficult to smelt have been associated with the production of iron of poor quality.

The difficulty of the situation is that we have no proven yardstick for quality aside from ordinary analysis. Uniformity in analysis is recognized as being important, but the difficulty of changing the open-hearth practice when the iron analysis varies widely may not always be fully appreciated. Although the problem of correlating the characteristics of steel with those of pig iron is admittedly obscure, the effort of producers of quality steel to investigate all factors that may have a bearing on the final product is justified.

This report contains data on the oxides in several hundred casts of basic iron produced in a furnace during the course of normal operation on Lake ores. Incidental to the study of the oxides in the iron, it was desirable to follow closely the temperature of the iron. The effect of temperature of the iron upon the silicon and sulphur present is discussed. A general relation between the basicity of the slag and the sulphur in the metal was developed. The amount and composition of oxides in the hot metal and in the steel bath during various intervals between melt-down and tap are discussed. Heats of rimmed steel, killed steel, and semikilled steel were investigated. The hot metal on individual heats was either all taken from a mixer or consisted partly of direct metal and partly of metal from the mixer. Samples of the iron for oxide determinations were

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taken from transfer ladles just before charging into the open hearth. All samples from the steel bath were taken in pairs. One was allowed to rim in the sample mold while the other was killed with aluminum. The conclusions reached are summarized later in the paper.

### TEMPERATURE MEASUREMENTS OF THE IRON

The temperature prevailing in the shaft as well as in the crucible has an important bearing upon the iron product. Emphasis was placed upon the temperature of the metal in the runner, as this appeared to offer a key to the over-all temperature effects. The effect of absolute and uniform tuyere temperatures, slag temperatures, and temperatures in the shaft is reflected in the temperature of the iron. Under proper atmospheric conditions and with proper emissivity corrections metal temperatures of iron in the runner can be followed satisfactorily with an optical pyrometer. Wensel and Roeser<sup>1</sup> have taken simultaneous optical-pyrometer readings and observations with platinum to platinum-rhodium thermocouples on streams of iron. For true temperatures above 1375° C. or 2507° F. their work indicated an emissivity of approximately 0.4 for a stream of iron. This corresponds to a correction of 230° at 2552° F. and 284° at 2912° F. true temperature. A change in emissivity was observed below 2507° F., which is below the normal temperature of iron in the blast-furnace runner. In the present investigation the temperature of iron in the runner was measured with platinum to platinum-rhodium thermocouples, for several reasons. The temperature of the iron as tapped from a furnace varies during a single cast. A continuous record of the entire cast is necessary, therefore, to arrive at an average temperature. While a large number of properly timed pyrometer readings is entirely feasible, an automatic, continuous record is preferable. Such a record eliminates the personal equation that would be a factor in observing five daily casts on a furnace. Fumes and smoke in the cast house often make it difficult to get satisfactory optical pyrometer readings.

*Temperature-measuring Equipment.*—The temperature of the iron in the runner was obtained by a 24-in. platinum to platinum-rhodium thermocouple encased in a porcelain protection tube. The porcelain tube was placed in a 24 by 3-in. graphite electrode bored with a 1-in. drill. Compensating lead wires were used to connect the thermocouples with an indicating potentiometer or a recorder. Fig. 1 shows the holder for immersing the protected thermocouple in the stream of iron. The 3-in. graphite tube fits inside a 10-in. length of 3-in. pipe, which is held between two vertical steel strips spaced about 3 in. apart. The vertical steel strips are welded to a heavy steel baseplate. A dam of sand, visible

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<sup>1</sup> References are at the end of the paper.



upon close examination of Fig. 1, was made just below the graphite tube. This dam was built to a height that provided immersion of 7 to 10 in. of the graphite protection tube. Toward the end of the cast, when the

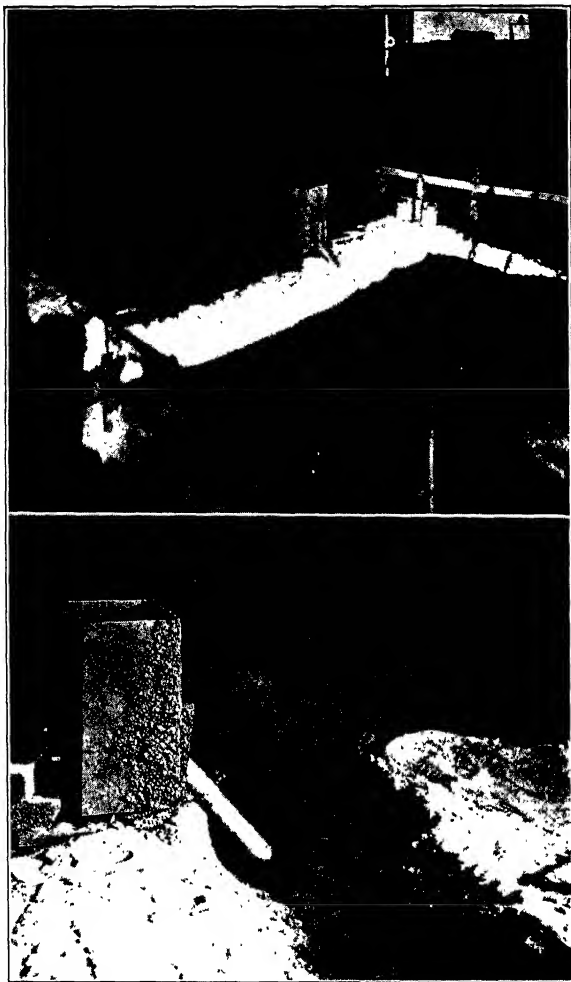


FIG. 1.—DEVICE FOR HOLDING NOBLE METAL THERMOCOUPLE IN BLAST-FURNACE RUNNER.

stream was small, the dam of sand was broken so that the iron drained away from the graphite tube.

*Optical-pyrometer Readings under Black-body Conditions.*—During preliminary work on measuring the temperature of the iron, the thermocouple readings were checked against simultaneous optical-pyrometer observations obtained by sighting on the closed end of a second graphite tube immersed in the iron adjacent to the tube protecting the thermo-

couple. Fig. 2 shows a set of such simultaneous readings. The optical-pyrometer readings under black-body conditions averaged  $12^{\circ}$  F. lower than those obtained with the thermocouple. Similar observations were made on about 25 other casts. Toward the end of cast 2123, the flow of iron receded sharply, then increased, and fell off again. Readings taken during a slow flow of iron are low. Such low readings are due to a drop in the temperature of the iron and also to shallow immersion. When

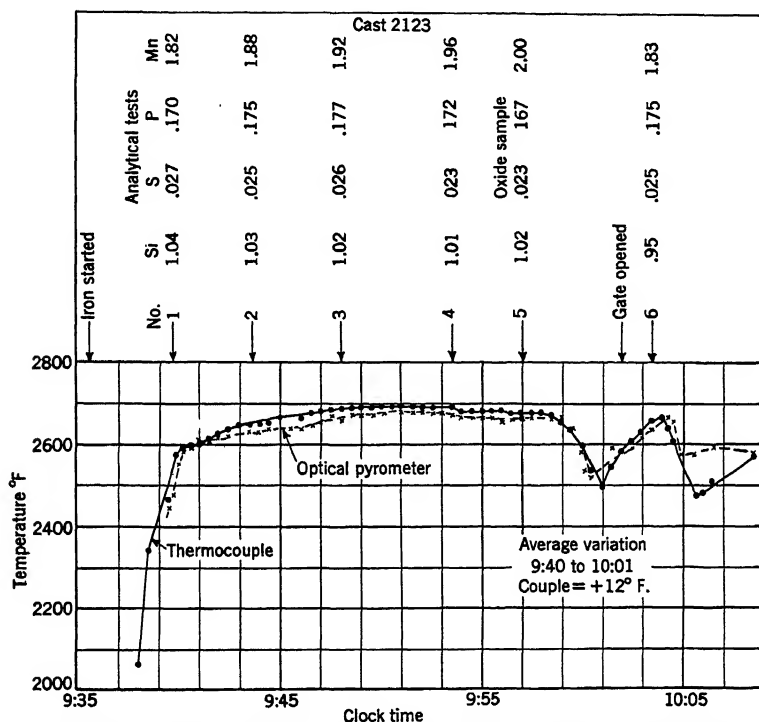


FIG. 2.—METAL TEMPERATURES WITH NOBLE METAL THERMOCOUPLES AND WITH OPTICAL PYROMETER (BLACK-BODY CONDITIONS).

a continuous temperature record of a cast is obtained with a recording instrument, such periods can be discarded in arriving at the average temperature of the cast. Observations on small or slow-flowing casts due to a small taphole or other causes are likely to be low. It is desirable, therefore, to have a record of the flow of iron and depth of immersion.

*Effect of Wall Thickness of Secondary Graphite Protection Tube upon Temperature Observations with Noble-metal Thermocouples.*—A primary porcelain tube encasing a noble-metal thermocouple and in turn protected by a thin-walled graphite tube undergoes a severe thermal shock when molten iron first comes in contact with the graphite. In following the temperature of several hundred consecutive casts, it was necessary to use a graphite tube with approximately 1-in. wall thickness to hold the cost of

protection tubes at a reasonable figure and to prevent the complete loss of thermocouples. Tests were made to determine the error introduced by conduction of heat away from the tip of a graphite tube with 1-in. walls when immersed 7 to 10 in. in the iron.

Observations were made on two casts using two new noble-metal thermocouples. One thermocouple was encased in a 3-in. graphite tube with 1-in. wall thickness and the other one in a 1 $\frac{1}{4}$ -in. graphite tube with  $\frac{1}{4}$ -in. wall thickness. Both tubes were immersed in the iron to a depth of from 7 to 10 in. As shown in Fig. 3, cast 2903 was longer than cast 2907. Therefore the flow of iron in cast 2907 was somewhat more rapid. In cast 2903, the recorder did not respond quickly to temperature changes. The temperature observed by means of the indicating potentiometer on both thermocouples indicates a conduction error on the

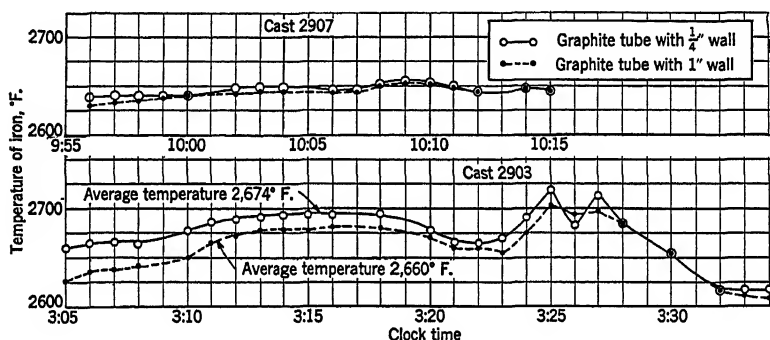


FIG. 3.—EFFECT OF WALL THICKNESS OF SECONDARY GRAPHITE PROTECTION TUBE UPON OBSERVED IRON TEMPERATURES IN THE BLAST-FURNACE RUNNER.

order of 14° F.; that is, the conduction of heat away from the tip of the large tube resulted in low readings. The readings with an optical pyrometer on cast 2903 averaged 6° F. below those obtained with the thermocouple in the thin-walled graphite tube. Atmospheric conditions were favorable for optical readings during this cast. The metal flow in cast 2907 was more rapid. The diameter of the large graphite tube had also been reduced above the level of the iron stream, owing to oxidation. Both factors reduced the conduction error. No claim is made for the accuracy indicated by the readings on this cast.

Considering the two casts, the data indicate that the conduction error may range from a few degrees to 20° F., with an immersion of 7 to 10 in. and varying rates of iron flow. Since the correction is small and relative temperatures are of chief concern, no correction was made in the observed temperatures. Although conditions were not favorable for optical-pyrometer readings during portions of these casts, particularly 2907, the agreement is fair. An emissivity factor of 0.4 was applied to the optical readings.

*Care of Thermocouples.*—Adequate protection of the thermocouples required that the primary protection tubes be inspected once each day. They were discarded as soon as any evidence of longitudinal cracks appeared. The thermocouples were inspected after use in about 10 casts and were annealed before being placed in service again. Whenever sections of new wire were welded into thermocouples, tests were made adjacent to the weld for parasitic currents. Rarely were they found to be off calibration by more than  $10^{\circ}$  to  $12^{\circ}$ .

### SULPHUR AND SILICON IN IRON

*Relation between Sulphur and Silicon and Temperature of the Iron.*—It is generally known that the silicon and sulphur in the iron are affected

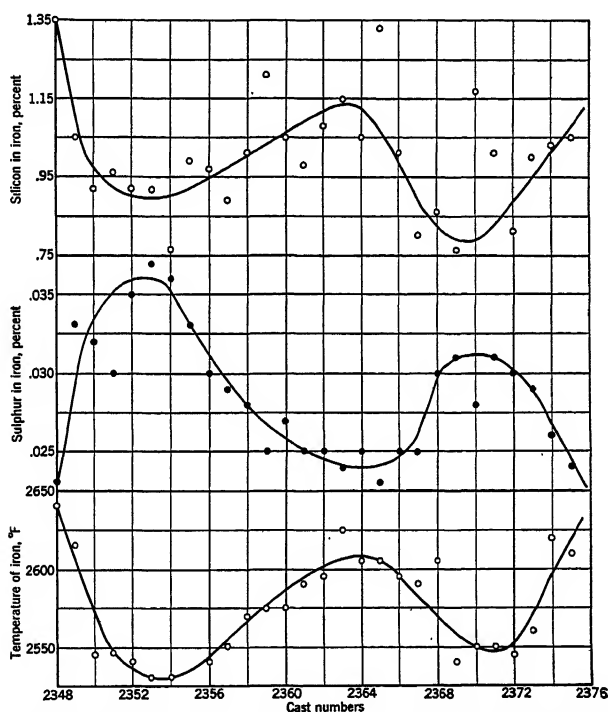


FIG. 4.—RELATION BETWEEN SILICON AND SULPHUR AND THE TEMPERATURE OF CONSECUTIVE CASTS.

by furnace temperatures. Normally, a rise in temperature of the slag and metal is accompanied by an increase in silicon and a decrease in sulphur. This relationship was borne out by temperature measurements on a large number of casts. While it usually held from cast to cast, it was more obvious during periods of gradual but persistent trends up or down in the temperature of the metal. This is illustrated in Fig. 4. The sulphur in the iron and the temperature of the iron are somewhat

more closely related than silicon content and temperature. The data indicate that the average relative temperature was followed closely by the thermocouple measurements. The period shown in Fig. 4 is not typical, as the silicon and sulphur normally fluctuated within rather narrow limits.

A general relation between average silicon and average sulphur in the iron and average temperature of 452 casts is given in Fig. 5. Casts were grouped according to average temperature increments of 20° F. Average results from a fairly large number of casts show a very consistent relationship between the temperature of the metal and silicon and sulphur.

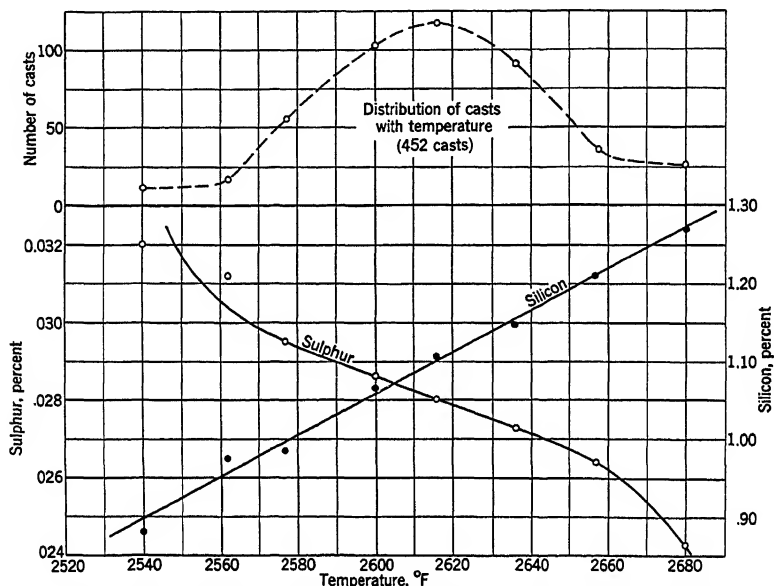


FIG. 5.—AVERAGE RELATION BETWEEN TEMPERATURE OF METAL AND SILICON AND SULPHUR.

Individual casts do not show any such agreement as indicated in Fig. 5, but when a group of casts is considered and other factors, such as the basicity of the slag, average approximately the same a definite relation exists. The silicon in the iron increased about 10 points (0.10 per cent) for each increase of 40° F. in the temperature of the metal. The tendency toward an S-shaped curve shows that below about 2575° C. the sulphur increases more rapidly as the temperature decreases. Similarly, the sulphur decreases more rapidly for temperatures above 2650° F.

There was a comparatively small number of casts in the extremes of the temperature range. Therefore the positions of the extremes of the sulphur-temperature curve are not established as definitely as the position of the remainder of the curve.

*Close Control of Sulphur and Silicon Requires Close Control of Temperature.*—The upper curve in Fig. 5 shows the distribution of casts in the

various ranges of temperature. The average temperature of about 70 per cent of the 452 casts falls within the range of 2600° to 2640° F., and the average temperature of about 80 per cent of the casts falls within a temperature range of 2580° to 2640° F. These data show the necessity of close temperature control to hold the sulphur and silicon within narrow limits. The figures given may not apply to other furnaces, but a similar study on other furnaces would show the most desirable temperature range for any given silicon and sulphur specifications.

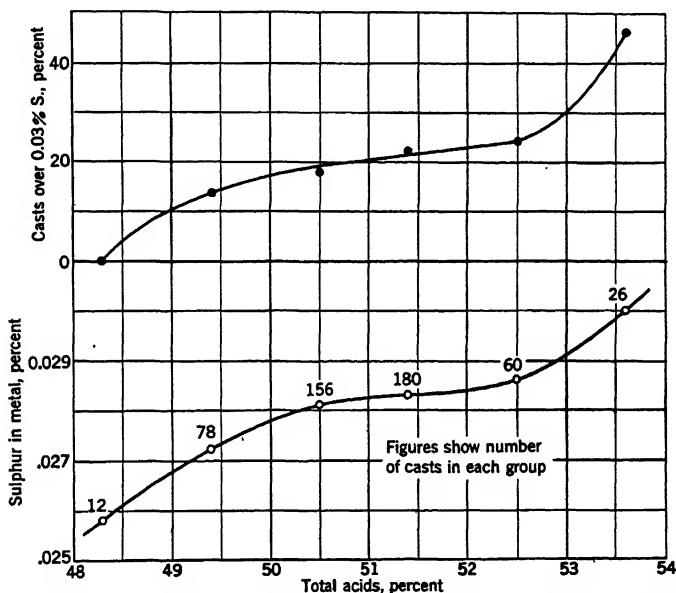


FIG. 6.—RELATION BETWEEN TOTAL ACIDS IN SLAG AND SULPHUR IN THE METAL.

To control the temperature of such a large-scale operation closely requires uniform raw materials. The most difficult problem is to maintain the same approach to uniformity with respect to gas distribution. If the gas distribution follows the same pattern the tendency will be towards uniform operation. The most effective means of more nearly attaining uniformity is through size preparation of raw materials. In general, changes in routine operation should be made as infrequently as possible.

*Effect of Total Acids in Slag upon Sulphur in Metal.*—The sulphur in the metal is a function of slag basicity as well as of temperature. Fig. 6 and Table 1 show the effect of total acids in the slag upon the sulphur in the metal, with the silicon in the metal and the temperature of the metal fairly constant. As shown in Fig. 6, desulphurization improves more rapidly as the total acids decrease below about 50 per cent. With total acids between 50 and 52.5 per cent, slag basicity is less important; tem-

perature being the main controlling factor. As the total acids increase above 52.5 per cent the sulphur increases more rapidly. That the section of the curve is flatter in the intermediate total acid range is borne out by the similar S-shaped curve that shows the relation between total acids and the percentage of casts in each range that contained over 0.03 per cent sulphur. It should not be concluded from the curves in Fig. 6 that all

TABLE 1.—*Effect of Total Acids in Slag on Sulphur in 512 Casts*

Number of Casts	Percentage of Total Casts <sup>a</sup>	Range Total Acids, Per Cent	Average Total Acids, Per Cent	Average Sulphur, Per Cent	Percentage of Casts <sup>b</sup> over 0.030 Per Cent Sulphur	Average Silicon, Per Cent	Average Cast Temperature, Deg. F.
12	2.3	47 to 49	48.3	0.0258	0	1.15	2,608
78	15.2	49 to 50	49.4	0.0272	14	1.10	2,622
156	30.5	50 to 51	50.5	0.0281	18	1.09	2,616
180	36.2	51 to 52	51.4	0.0283	22	1.10	2,629
60	11.7	52 to 53	52.5	0.0286	24	1.10	2,619
26	5.1	53+	53.6	0.0300	46	1.10	2,617

<sup>a</sup> Percentage of total casts in each range of total acids in the slag.

<sup>b</sup> Percentage of casts over 0.030 per cent sulphur in each range of total acids in the slag.

that is required to produce iron in the 0.025 per cent sulphur range is to decrease the total acids to about 48 per cent. Loss of tonnage, higher fuel consumption, and more irregular operations are normally encountered to some degree in this range of total acids.

#### PREVIOUS WORK ON OXIDES IN PIG IRON

The amount of oxides and silicates in steel and pig iron is often expressed in terms of total oxygen, which refers primarily to oxygen combined in the form of oxides or silicates. The results of some previous work are summarized in Table 2.

Eckman, Jordan, and Jominy<sup>2</sup> determined the total oxygen on 12 samples of charcoal iron for comparison with the oxygen content of coke iron. Thirty-gram samples were heated 1 hr. at 1450° to 1500° C. in a high-frequency vacuum furnace. The total oxygen, calculated from the weight of water, carbon monoxide, and carbon dioxide evolved, ranged from nil to 0.010 per cent, averaging 0.002 per cent for 12 samples of charcoal iron. Iron made with coke as a fuel ranged in total oxygen from nil to 0.014 per cent, averaging 0.005. In discussing this paper, McKenzie cited a highly oxidized cast iron that contained 0.018 per cent total oxygen by the vacuum-fusion method.

Reeves<sup>3</sup> has reported a badly oxidized iron that contained, according to the fractional vacuum-fusion method, 0.047 per cent total oxygen. Most of the oxygen was evolved during treatment for the FeO and MnO

fractions, which indicates that MnO and FeO were far from equilibrium with the silicon and carbon in the sample.

Oberhoffer and Piwowsky<sup>4</sup> determined the total oxygen in coke iron, Swedish charcoal iron, and iron melted in a cupola. Ten-gram samples were heated 30 min. in a porcelain tube at 1200° C. under vacuum.

TABLE 2.—*Oxide Content of Pig Iron*

Investigator	Type of Iron	Method for Determining Oxides	Range of Total Oxygen, Per Cent	Average Total Oxygen, Per Cent
Johnson.....	Charcoal	Hydrogen reduction	0.009 to 0.065	0.026
Eckman, Jordan, and Jominy.	Charcoal	Vacuum fusion	nil to 0.010	0.002
	Coke	Vacuum fusion	nil to 0.014	0.005
Oberhoffer and Pi- wowsky.	Charcoal	Vacuum fusion in porce- lain tube	0.012 to 0.033	0.023
	Charcoal (white)	Vacuum fusion in porce- lain tube		0.015
	Charcoal (mottled)	Vacuum fusion in porce- lain tube		0.021
	Charcoal (gray)	Vacuum fusion in porce- lain tube		0.028
	Coke	Vacuum fusion in porce- lain tube	0.012 to 0.036	0.022
	Cupola melted	Vacuum fusion in porce- lain tube	0.021 to 0.047	0.035
Reeves.....	Cast (badly oxidized)	Fractional vacuum fu- sion		0.047
Jordan.....	Gray (badly oxidized)	Vacuum fusion		0.018
Herty and Gaines.	Basic	Dickenson	0.003 to 0.040	0.011

The total oxygen in the coke iron ranged from 0.012 to 0.036 per cent and averaged 0.022. Features of blast-furnace practice, such as blast temperature, burden, and type of slag produced, gave no indication of the cause for variations in the oxides in the iron. Swedish charcoal irons ranged from 0.012 to 0.036 and averaged 0.023 per cent total oxygen. White-charcoal irons studied averaged 0.015, mottled 0.021, and gray charcoal iron 0.028 per cent total oxygen, which shows an increase in oxygen as the silicon increased. Samples of iron that had been melted in a cupola ranged from 0.021 to 0.047 per cent in total oxygen with three high samples (0.056, 0.059 and 0.052 per cent) omitted.



Bardenheuer and Reinhardt<sup>5</sup>, in studying the influence of the smelting process on the crystallization and mechanical properties of gray cast iron, have reported 0.002 to 0.008 per cent oxygen on samples of gray iron superheated under slags high in ferrous oxide.

Herty and Gaines<sup>6</sup> investigated the oxides in basic pig iron and their elimination in the basic open-hearth furnace. The silicates in 26 casts of iron, as determined by the Dickenson method, ranged from a trace to 0.137 and averaged 0.025 per cent total silicates. From the average analysis of the silicates this is equivalent to 0.011 per cent total oxygen.

### OXIDES IN BASIC PIG IRON

The difficulties encountered in investigating the oxides in pig iron are partly responsible for the scarcity of data on the subject. Substantial progress has been made in developing methods for determining the amount of nonmetallic matter in steel, but the results achieved by investigators using the same or different methods may vary considerably. The inclusions are present in small concentrations, and the amount of sample that can be used in some methods is limited. Since the inclusions are not in solution but are held mechanically, segregation may lead to sporadic results. Pig iron offers even greater difficulties than steel and has received less study. The difficulties and limitations of the problem are recognized in presenting the data reported herein.

*Method Used for Determining Oxides.*—The electrolytic method was selected, for several reasons. Comparatively large samples are used in the extraction, the composition of the residue can be determined, and a large number of samples can be analyzed fairly rapidly and at comparatively small cost. The method has been used successfully in determining the oxides in steel and, with certain precautions, is adaptable to pig iron. A description of the method is given in the Appendix.

*Method of Sampling for Oxides.*—Several hundred consecutive casts of basic iron from the Inland Steel Company's No. 2 blast furnace were sampled to determine the amount and composition of oxides in the iron. Samples taken from the runner were poured into a split-metal mold, making a solid piece of iron about 6 by 2 by 1 in. The mold was heated over the edge of the stream of iron before the sample was taken. As soon as the sample had been poured the mold was covered with sand. This procedure promoted graphitization and facilitated the preparation of coupons or metal strips used in electrolytic extraction of the oxides. The coupons were sawed or machined from the central and lower portion of the sample to avoid the effect of surface contamination.

*Oxide Content of Basic Iron.*—The results of oxide determinations on samples from 475 casts, grouped according to total oxides, are summarized in Table 3, which shows the distribution of casts with respect to total oxides and also gives average results on the amounts and composition

of the oxides present. The data represent the results of two tests conducted about six weeks apart, during which 281 and 194 casts, respectively, were made.

TABLE 3.—*Summary of Oxides in Basic Pig Iron*

Number of Casts	Percent- age of Total Casts	Percent- age Total Casts Cumu- lative	Range of Total Oxides, Per Cent	Average Total Oxides, Per Cent	Oxides in Sample, Per Cent				Oxides in Ex- traction Resi- due, Per Cent			Cast		
					SiO <sub>2</sub>	MnO	FeO	Total O <sub>2</sub>	SiO <sub>2</sub>	MnO	FeO	Tem- per- ature, Deg. F.	Si, Per Cent	S, Per Cent
FIRST TEST PERIOD														
68	24.2	24.2	0.012 to 0.025	0.019	0.005	0.004	0.010	0.006	26.3	21.1	52.6	2600	1.04	0.028
88	31.3	55.5	0.025 to 0.050	0.037	0.007	0.006	0.024	0.010	18.9	16.2	64.9	2614	1.08	0.028
49	17.45	72.95	0.050 to 0.075	0.062	0.008	0.009	0.045	0.016	12.9	14.5	72.6	2617	1.11	0.028
29	10.30	83.25	0.075 to 0.100	0.085	0.008	0.013	0.064	0.021	9.4	15.3	75.3	2607	1.08	0.027
47	16.75	100.00	0.10 to 0.30	0.160	0.014	0.008	0.138	0.040	8.8	5.0	86.2	2616	1.10	0.028
Weighted average..				0.063	0.008	0.007	0.048	0.017	12.7	11.1	75.2	2610	1.08	0.028
SECOND TEST PERIOD														
56	28.9	28.9	0.011 to 0.025	0.019	0.005	0.004	0.010	0.006	26.9	19.0	54.1	2628	1.12	0.029
70	36.0	64.9	0.025 to 0.050	0.035	0.009	0.006	0.020	0.010	27.5	16.7	55.8	2626	1.15	0.027
32	16.5	81.4	0.050 to 0.075	0.063	0.015	0.008	0.040	0.019	23.7	13.0	63.3	2620	1.12	0.028
20	10.3	91.7	0.075 to 0.10	0.090	0.019	0.011	0.060	0.026	20.4	12.8	66.8	2628	1.18	0.028
16	8.3	100.0	0.10 to 0.31	0.148	0.021	0.015	0.112	0.040	15.6	12.2	72.2	2628	1.20	0.028
Weighted average...				0.050	0.011	0.007	0.032	0.015	22.0	14.0	64.0	2626	1.14	0.028

Similar results were obtained for the two tests. As the total oxides increased, the percentage of FeO in the inclusions increased, and the percentages of SiO<sub>2</sub> and MnO decreased. This is particularly true of the first test period. The oxide residues in the first period were less siliceous than those in the second period, the average being 12.7 and 22.0 per cent SiO<sub>2</sub>, respectively. When examined under the microscope some inclusions were found to contain spherical bodies of iron. Metal thus surrounded by oxides would be likely to carry through to the analyzed residue and therefore may be the cause for the apparent increase in FeO as the total oxides increase.

The results of oxide determinations on samples taken during the second test period are more nearly uniform than those taken during the first period. This is attributed to better sampling of the iron in the second period, which smoothed out variations due to large segregates. About 30 per cent of the casts in this period ranged from 0.011 to 0.025 per cent total oxides and averaged 0.019 per cent, which is equivalent to 0.006 per cent total oxygen. Slightly more than 80 per cent of the casts contained under 0.075 per cent total oxides. The 194 casts in the second period averaged 0.050 per cent total oxides, distributed as follows: 0.011 per cent  $\text{SiO}_2$ , 0.007 per cent  $\text{MnO}$ , and 0.032 per cent  $\text{FeO}$ . This is equivalent to an average of 0.015 per cent total oxygen. This average result is somewhat higher than the average of 0.011 per cent total oxygen obtained by Herty and Gaines by means of the Dickenson method (Table 2). Owing to solubility of  $\text{MnO}$  and particularly  $\text{FeO}$  in cold 10 per cent nitric acid, results obtained with the Dickenson method would be low. It is more satisfactory for  $\text{SiO}_2$  than for  $\text{FeO}$  and  $\text{MnO}$ . Except for a few determinations by the vacuum-fusion method on what was reported as badly oxidized samples of cast iron, the results obtained in this investigation are higher than those obtained by the vacuum-fusion method<sup>2,3</sup>. The results of Oberhoffer and Piwowarsky<sup>4</sup> on charcoal and coke iron are considerably higher than those obtained with Scott's electrolytic method<sup>5</sup>. These investigators reported average values of 0.023 per cent total oxygen for charcoal iron and 0.022 per cent total oxygen for coke iron.

*Oxides, Silicon and Sulphur in the Iron and Cast Temperatures.*—No relation was found between the amount of oxides in the iron and its temperature in the runner. The results in Table 3 show no definite trend in temperature in either test period corresponding to increasing concentrations of oxides. In the second test period the average temperatures are surprisingly constant for groups of casts that average 0.019 to 0.148 per cent total oxides. The average temperature of the metal remained constant, although the average amount of oxides increased about eightfold. There is a slight tendency for the silicon in the iron to increase as the total oxides increase, but the increase in silicon is too small to be significant. The average sulphur in the iron varied only one point for groups of casts that average from 0.019 to 0.160 per cent total oxides. Occasional casts containing from 0.033 to 0.037 per cent sulphur showed no tendency to be higher in total oxides. The data show no justification for assuming that the iron will contain more oxides if it is high in sulphur. Since the oxides are not related to the temperature of the iron, one would not expect them to vary with the silicon or the sulphur, as the amounts of these elements in the iron are directly related to temperature.

*Variations in Composition of Oxides in Individual Casts.*—The summarized data in Table 3 do not show the variation in the composition of the oxide residues obtained from individual casts. Although  $\text{FeO}$  was the

major oxide in most casts,  $\text{SiO}_2$  equaled or exceeded the  $\text{FeO}$  in occasional casts. Small amounts of  $\text{Al}_2\text{O}_3$  were found in only a few casts. The extraction residue contained small amounts of  $\text{TiO}_2$  that did not vary greatly. The fact that  $\text{Al}_2\text{O}_3$  was not present in the more siliceous oxides indicates that the silicon was not due to entrapped slag. On the basis of the effect of the iron upon open-hearth practice, it is important to note that  $\text{FeO}$  is the principal oxide found in the iron. The percentage of  $\text{SiO}_2$  and  $\text{MnO}$  in the inclusions varied considerably from one sample to another. Determinations on a large number of samples are necessary, therefore, to arrive at any conclusions as to the composition of the oxides in iron. On the basis of the tendency of oxides in the iron to persist through the open-hearth process, the  $\text{SiO}_2$  content is more important than the  $\text{FeO}$  and  $\text{MnO}$  contents. The oxide residues obtained in this investigation were less siliceous than the residues obtained by Herty and Gaines. The  $\text{SiO}_2$  in the residues of the last test period averaged 22 per cent compared to an average of 47 per cent for the work of Herty and Gaines.

*Physical Character of Oxides Extracted from Basic Pig Iron.*—The inclusions obtained consisted of comparatively large angular pieces interspersed with small black or reddish brown particles arranged in clusters that could be broken readily. Occasionally white grains of silica appeared in the residue, but the larger distinct particles were usually reddish brown or black. The residues from samples high in oxides required a much longer time for filtering and washing preparatory to burning off the graphite, which indicates that finely divided material made up the major portion of the residue. There was also some indication that the graphite contained in such residues was more finely divided. All high samples showed evidence of gritty material when moved around on the bottom of a beaker with a glass stirring rod.

*Microscopic Examination of Pig Iron for Inclusions.*—Eight samples of pig iron were examined for inclusions, at 50 and 1000 diameters. Photomicrographs at 50 diameters appear in Figs. 7 and 8. A large inclusion is shown in Fig. 8 and a small triangular one in the lower left corner of Fig. 7. The large inclusion shown in Fig. 8 is of interest, as the presence of such large segregates in a section of metal analyzed for oxides would result in high oxide content and tend to give erratic results. There is no apparent relation between the form of the graphite and the amount of oxides determined by electrolytic extraction.

Small, gray, angular or hexagonal inclusions visible at 1000 diameters characterize all eight samples (Fig. 10). These inclusions are too small for identification. The large inclusion shown in Fig. 9 illustrates the difficulty of polishing samples without dislodging inclusions of the more friable and less siliceous type. This sample contained a large number of such inclusions, which were lost during polishing. The fragment retained was too small for identification, but the extreme friability indicates high  $\text{FeO}$  content.

One large inclusion contained particles of metallic iron, which indicated that it had been molten. Iron thus encased may account for the unusually high iron content of occasional samples, usually extremely high in total oxides. Metallic iron in an inclusion would not be eliminated during electrolytic extraction or during the copper sulphate treatment to eliminate metallic iron from the extraction residue. Figs. 11

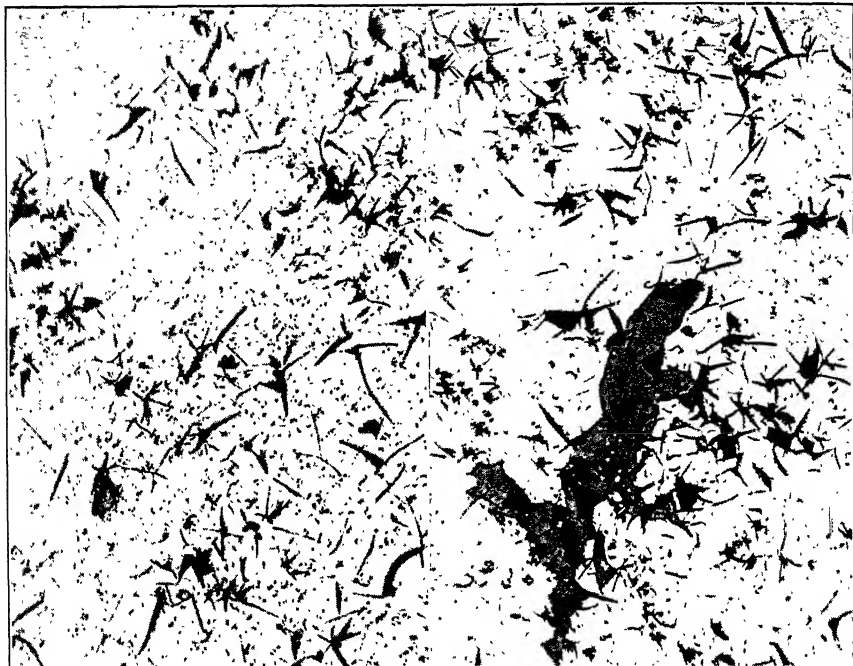


FIG. 7. FIG. 8.  
FIGS. 7 AND 8.—DISTRIBUTION OF GRAPHITE IN BASIC PIG IRON.  
Fig. 7, Cast 2443. Fig. 8, Cast 2483. Unetched.  $\times 50$ .

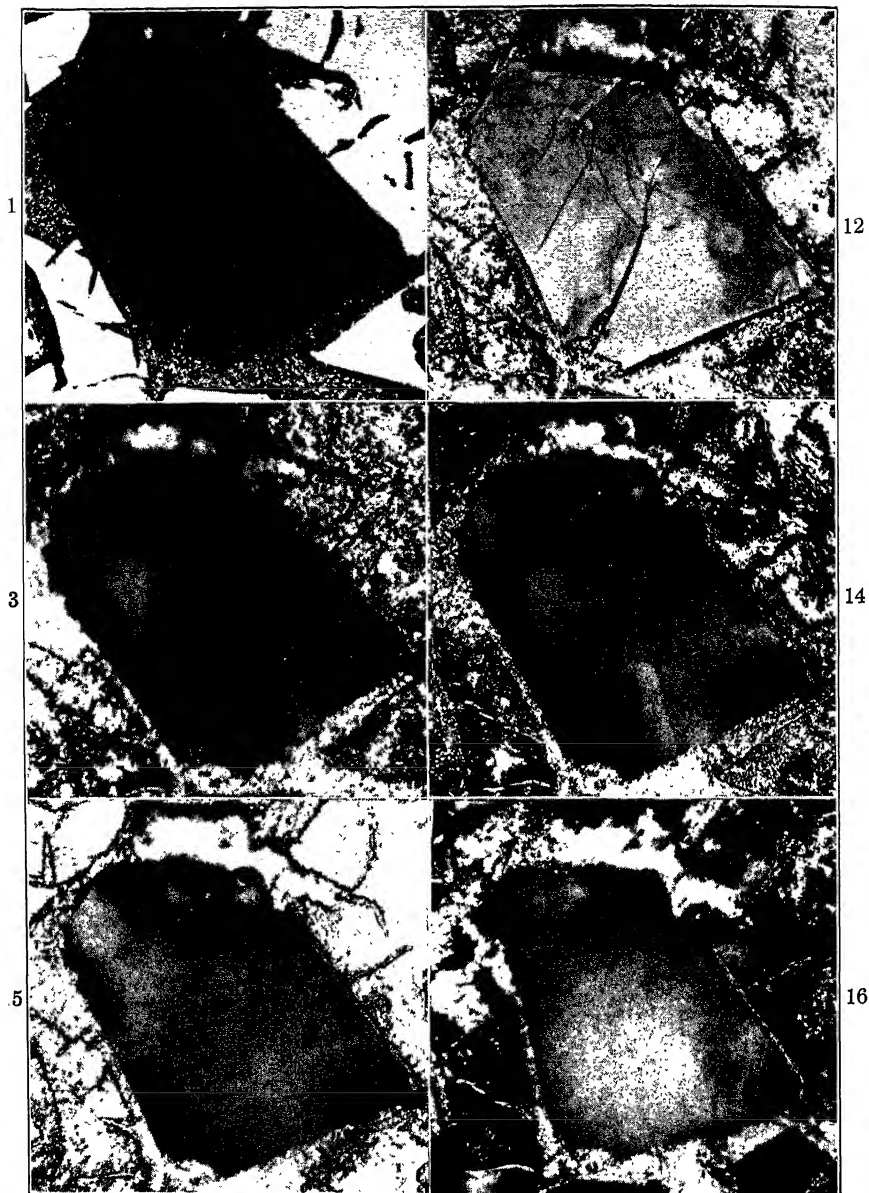
to 16 show a large inclusion before and after the application of Wohrman's identification etches. The inclusion is largely  $\text{SiO}_2$  with some  $\text{MnO}$  and possibly traces of  $\text{FeO}$  and  $\text{MnS}$ .

No relation was found between the number of small inclusions and the oxide content of the samples. Samples containing large inclusions were generally high in total oxides. Although microscopic study does not offer a satisfactory means of determining the amount of oxides in iron, it does show that inclusions are present and that they may occur as large segregates.

*Effect of Additions of Iron Ore, Sinter, Roll Scale, Ferric Oxide and Sponge Iron on Oxides in Pig Iron.*—Several attempts were made to introduce oxides into molten pig iron by additions of materials containing iron



FIG. 9. FIGS. 9 AND 10.—INCLUSIONS IN BASIC PIG IRON.  
Fig. 9, Cast 2309. Fig. 10, Cast 2443. Unetched.  $\times 1000$ .



FIGS. 11-16.—STRUCTURE AND INCLUSIONS AS SHOWN BY VARIOUS ETCHING REAGENTS.

Fig. 11.—Cast 2399. Unetched.

Fig. 12.—Cast 2399. Etched 10 sec. in 10 per cent nital.

Fig. 13.—Cast 2399. Etched 5 min. in 10 per cent chromic acid.

Fig. 14.—Cast 2399. Etched 5 min. in boiling sodium picrate.

Fig. 15.—Cast 2399. Etched 10 min. in saturated solution stannous chloride in alcohol.

Fig. 16.—Cast 2399. Etched 10 min. in aqueous solution of hydrofluoric acid.

Original magnification 500; reduced  $\frac{3}{4}$  in reproduction.

TABLE 4.—*Oxides in Pig Iron before and after Additions of Iron Ore, Sinter, Roll Scale, Ferric Oxide and Sponge Iron*

Oxides in Sample, Per Cent						Oxides in Residue, Per Cent			
Sample	SiO <sub>2</sub>	MnO	FeO	Al <sub>2</sub> O <sub>3</sub>	Total Oxides	SiO <sub>2</sub>	MnO	FeO	Al <sub>2</sub> O <sub>3</sub>
MELTS IN 100-LB. LADLE									
Before ore.....	0.0082	0.0025	0.0071	nil	0.0178	46.07	14.04	39.89	
After ore.....	0.0078	0.0026	0.0066	nil	0.0169	49.15	15.89	34.96	
Before sinter.....	0.0038	0.0096	0.0586	nil	0.0720	5.28	13.33	81.39	
After sinter.....	0.0100	0.0036	0.0189	nil	0.0323	30.96	11.15	57.89	
Before scale.....	0.0551	0.0284	0.1694	0.0115	0.2644	20.84	10.74	64.07	4.35
After scale.....	0.0145	0.0142	0.0318	nil	0.0505	27.71	9.93	62.36	nil
MELTS IN INDUCTION FURNACE									
Before Fe <sub>2</sub> O <sub>3</sub> .....	0.0030	0.0026	0.0180	nil	0.0236	12.71	11.02	76.27	
After Fe <sub>2</sub> O <sub>3</sub> .....	0.0046	0.0021	0.0150	nil	0.0218	21.10	9.63	69.27	
Before Fe <sub>2</sub> O <sub>3</sub> .....	0.0030	0.0026	0.0180	nil	0.0236	12.71	11.02	76.27	
After Fe <sub>2</sub> O <sub>3</sub> .....	0.0080	0.0036	0.0231	nil	0.0347	23.05	10.37	66.58	
Before sinter.....	0.0030	0.0026	0.0180	nil	0.0236	12.71	11.02	76.27	
After sinter.....	0.0245	0.0013	0.4056	nil	0.4314	5.68	0.30	94.02	
Before ore.....	0.0030	0.0026	0.0180	nil	0.0236	12.71	11.02	76.27	
After ore.....	0.0048	0.0012	0.0235	nil	0.0295	16.27	4.07	79.66	
SYNTHETIC PIG IRON FROM ADDITIONS OF FERROMANGANESE AND FERROSILICON TO PURE IRON									
Synthetic pig iron.....	0.0205	0.0006	0.4080	0.0031	0.4312	4.74	0.14	94.4	0.72
OXIDES IN CHARCOAL IRON BEFORE AND AFTER ADDITIONS OF SPONGE IRON: $\left(\frac{\text{CHARCOAL IRON}}{\text{SPONGE IRON}} = \frac{3}{1}\right)$									
Charcoal iron:									
Sample 1.....	0.0101	0.0019	0.0124	nil	0.0244	43.39	7.75	50.86	
Sample 2.....	0.0072	0.0014	0.0108	nil	0.0199	37.11	7.22	55.67	
Average.....	0.0087	0.0017	0.0116	nil	0.0219	39.25	7.48	53.27	
OXIDES IN IRON AFTER ADDITION OF SPONGE IRON									
Sample 1.....	0.0077	0.0012	0.0141	nil	0.0230	33.48	5.22	61.30	
Sample 2.....	0.0095	0.0013	0.0168	nil	0.0276	30.80	4.71	64.49	
Sample 3.....	0.0034	0.0007	0.0097	nil	0.0138	24.66	5.01	70.35	
Average.....	0.0068	0.0011	0.0135	nil	0.0215	31.78	5.14	63.08	
ANALYSIS OF CHARCOAL IRON BEFORE AND AFTER ADDITION OF SPONGE IRON									
	Si	S	Mn	P					
Before.....	3.53	0.027	0.59	0.195					
After.....	1.98	0.023	0.41	0.160					



unreduced material that reach the crucible, it would be possible to increase the oxides in molten pig iron by contact with such materials as ore, roll scale and sinter.

In the first series of tests reported in Table 4, iron ore, sinter and roll scale were added to 100 lb. of metal held in a small foundry ladle. Each ladle of iron was sampled and several pounds of one of the three materials was stirred into the iron. After the reaction was complete another sample was taken. Additions of sinter and roll scale decreased the oxides in the iron, whereas the iron ore had little effect. The elimination of oxides by the addition of sinter and roll scale is attributed to the fact that the iron to which these materials were added was unusually high in oxides. Substantial amounts of silicon and manganese were eliminated, so that some removal of oxides by a fluxing action seems probable. Considerable kish or graphite separated from the iron. This may have had a cleansing action. In the two tests in which a substantial reduction of oxides occurred, the residue was more siliceous after the treatment.

In the second series of tests, also reported in Table 4, chemically pure ferric oxide, sinter and roll scale were added to melts of the same iron held in an induction furnace. Twenty grams of ferric oxide was added to 760 grams of iron in the first test in this series. The oxide content of the iron did not change appreciably. When the addition of hematite was increased to 30 grams the total oxides increased from 0.0236 to 0.0347 per cent (Table 4). The largest increase in oxides resulted from the addition of sinter (0.0236 to 0.4314 per cent total oxides). The addition of iron ore produced a slight increase in the total oxides.

The temperature of the iron in the tests made in the induction furnace was restored after the additions were made, whereas the iron fell off steadily in temperature while being held in the foundry ladle. This may account for the loss of oxides in one case and the increase in the other. Microscopic examination of the inclusions in iron shows a tendency for them to be associated with graphite. It seems probable that the separation of graphite has a cleansing action. A synthetic pig iron made by adding ferromanganese and ferrosilicon to pure iron wire melted in an induction furnace was unusually high in FeO and total oxides. The oxide content of the fine wire could not be determined, but it was probably high.

About 110 grams of sponge iron was added to 290 grams of charcoal iron. Assuming that no silicon was introduced by the sponge iron, the silicon in the iron would decrease from 3.53 to 2.56 per cent by dilution. It was found to be 1.98 by analysis, which shows an appreciable loss of silicon by oxidation. Average results on the oxides in two samples of the original charcoal iron are very close to the average of three samples of the final melt. There was little change either in the amount or composition of the oxides (Table 4).

The results in Table 4 as a whole indicate that additions of oxides to pig iron in sufficient amounts to oxidize substantial amounts of silicon will not necessarily increase the amount of oxides in the iron. In two of eight tests the oxides increased by a substantial amount. In the other tests there was little change or a substantial decrease. The oxide residue

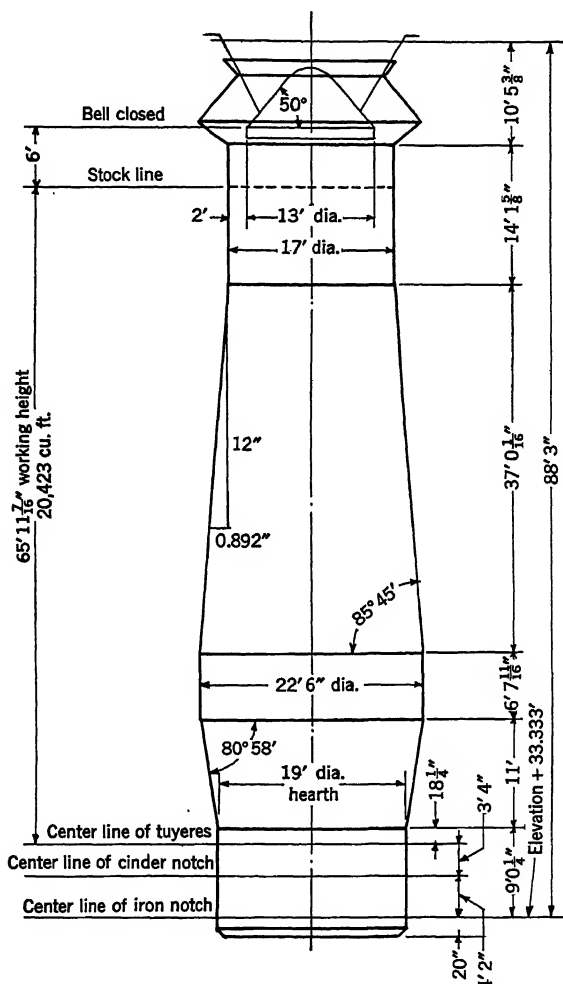


FIG. 17.—LINES AND DIMENSIONS OF NO. 2 BLAST FURNACE.

was more siliceous in most cases after the addition of oxides to the iron. The conditions governing the retention of oxides involve a number of factors, such as fluxing, coalescence into large particles, elimination of graphite, shape of the particle, and viscosity and temperature of the metal. In general, conditions are not favorable for the retention of oxides in pig iron. Contact between the iron and unreduced material

does not appear to be the cause for occasional casts of iron unusually high in oxides.

*Furnace Practice and Oxides in Basic Pig Iron.*—The lines and dimensions of the blast furnace are given in Fig. 17. A careful study was made

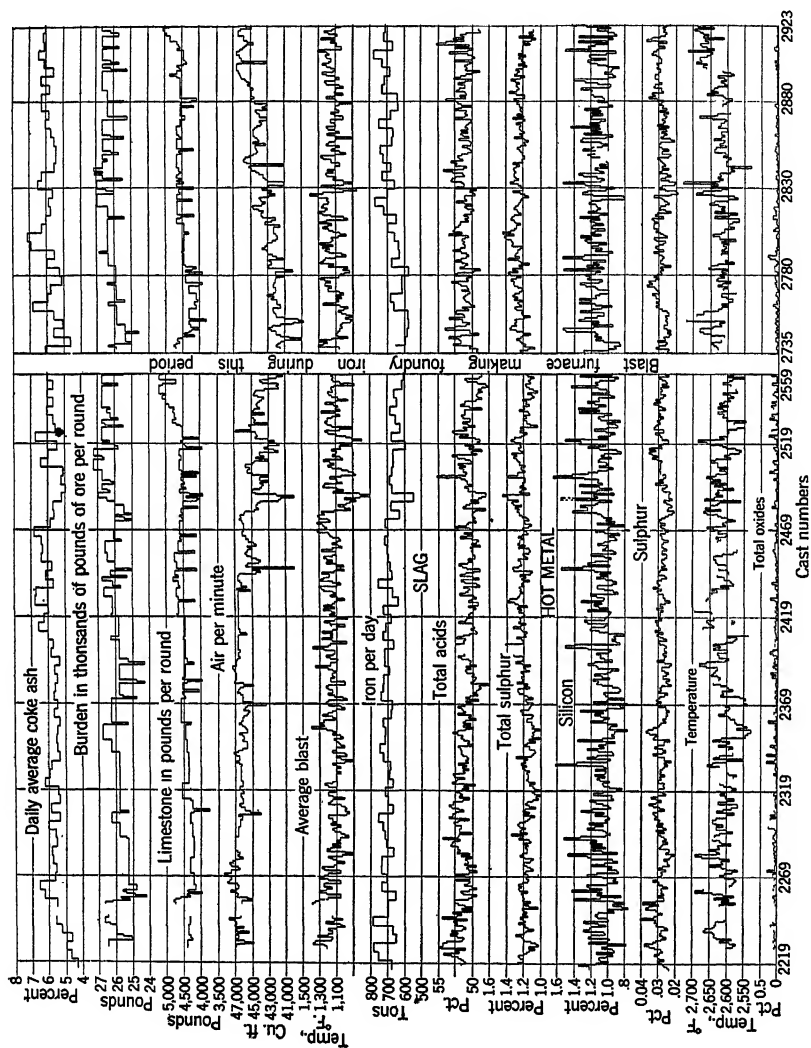


FIG. 18.—FURNACE PRACTICE AND OXIDES IN BASIC PIG IRON.

of all the important phases of furnace practice to determine the cause for variations in the oxides in the iron. Charts showing burden changes made about 8 hr. before cast, blast temperature, cubic feet of wind blown, FeO in the slag, total acids in the slag, total burden, and uniformity of top pressure were followed from cast to cast over several months. A portion of the operating data studied in relation to the oxides in the iron

is shown graphically in Fig. 18. There was no consistent correlation between any of these phases of practice and the oxides in the iron. During some periods the oxides increased as the burden was gradually increased. At other times high oxide content accompanied large changes in silicon, but this was not always true.

The silicon in the iron is an index of uniformity of operation. Table 5 shows a tendency toward a greater variation in the silicon when the iron contained more than 0.10 per cent total oxides. The last column of figures in this table gives the average change up or down in the silicon in

TABLE 5.—*Total Oxides in Basic Iron and Variations in Silicon Content*

Number of Casts	Range of Total Oxides, Per Cent	Average Total Oxides, Per Cent	Average Change in Silicon Content, <sup>a</sup> Per Cent
56	0.011 to 0.025	0.019	0.13
70	0.025 to 0.050	0.035	0.15
32	0.050 to 0.075	0.063	0.13
20	0.075 to 0.100	0.090	0.15
16	0.100 to 0.313	0.148	0.19

<sup>a</sup> Change in silicon from previous cast.

the iron as compared with the previous cast. For iron containing up to 0.10 per cent total oxides, which represents about 92 per cent of all the casts in the second test period, the variation in silicon is about the same for four groups of casts that average 0.019, 0.035, 0.064 and 0.086 per cent total oxides, respectively. Although the average oxide content varied almost fivefold, variations in silicon from cast to cast remained very nearly the same. For the highest oxide group the change in silicon from the previous cast averaged 19 points. Casts unusually high in oxides were associated with somewhat greater changes in the silicon content of the iron. Although moderate burdens and uniformity of operation appear to aid the production of iron lower in oxides, the problem is too complex to attribute the presence of oxides entirely to irregular operation. The humidity of the air apparently plays a minor part, as the oxides in the iron frequently fluctuated widely with no substantial changes in atmospheric conditions. Casts made in subzero weather were no lower in oxides than those made when it was raining.

#### OXIDES IN BASIC OPEN-HEARTH STEEL

The elimination of carbon in the open-hearth process depends upon introduction of FeO into the metal. Fig. 19 shows the relation between the carbon in the metal and the total oxygen as FeO obtained from samples killed with aluminum. These samples were taken during various stages of open-hearth heats between the time of melt-down and the addition of

deoxidizers. In the high-carbon range the points are more scattered, because of larger variations in temperature, slag conditions, and the lapse of time after ore additions. The position of the curve varies for different practices, depending largely on the FeO in the slag and the distance from equilibrium. The form of the curve, however, will be approximately the same. This curve does not represent equilibrium conditions but illustrates the general relation between FeO and carbon in the bath during the working and finishing periods of the heat. Below 12 per cent carbon the points lie fairly close to the curve because conditions approach a steady state more closely.

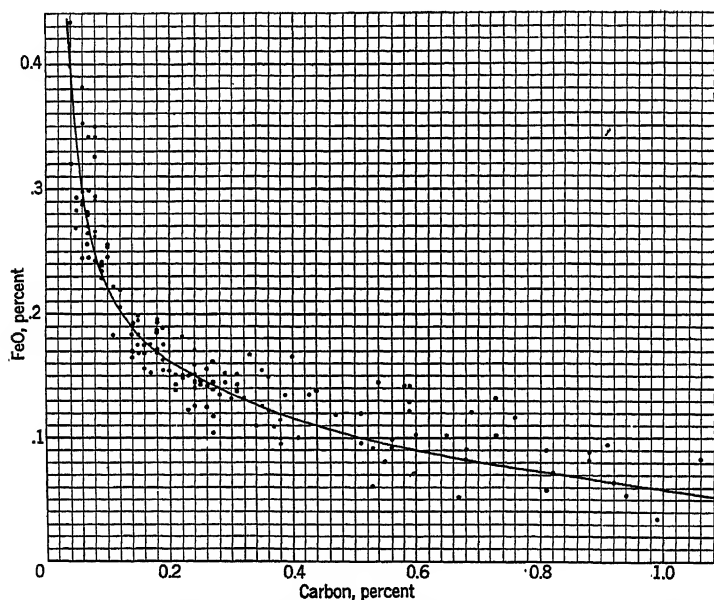


FIG. 19.—RELATION BETWEEN CARBON AND FERROUS OXIDE IN OPEN-HEARTH BATH BEFORE THE ADDITION OF DEOXIDIZERS.

As the carbon decreases to about 0.20 to 0.25 per cent, the FeO in the bath increases rather slowly. Below this range of carbon the FeO increases more sharply, becoming very rapid below about 0.10 per cent carbon.

In producing medium and high-carbon steel common practice is to reduce the carbon to about 0.20 per cent and increase it to the range desired in the finished steel by recarburizing with alloy additions, molten iron or some form of carbon. If the carbon is reduced to 0.20 per cent, the metal will contain on the order of 0.16 per cent FeO, which is about three times the average amount of total oxides found in pig iron (Table 3). If the carbon is reduced to the level of low-carbon rimming steel, the FeO in the bath will be five or six times the average total oxides found in basic

pig iron. Such large amounts of FeO favor the removal of  $\text{SiO}_2$ , as will be shown later. The oxides in the bath before the addition of deoxidizers consist almost entirely of FeO introduced into the bath to eliminate carbon. The amount of FeO in the bath is not rigidly fixed by the carbon, but the degree of oxidation of the bath is an inherent part of the open-hearth process (Fig. 19).

TABLE 6.—*Oxides in Low-carbon Steel at Tapping, at Pouring, in Test-mold Samples, and in Slabs*

Heat No.	Carbon, Per Cent	Ferrous Oxide in Furnace Bath, Per Cent	Ferrous Oxide in Ladle Sample, Per Cent	Total Residual Oxides in Test-mold Samples, Per Cent	Total Residual Oxides in Slab Samples, Per Cent	Silica in Test-mold Samples, Per Cent	Silica in Slab Samples, Per Cent
1	0.07	0.296	0.198	0.0228	0.0265	0.001	0.001
2	0.06	0.285	0.287	0.0405	0.0261	0.002	0.001
3	0.07	0.283	0.186	0.0508	0.0276	0.003	0.001
4	0.07	0.313	0.220	0.0326	0.0343	0.003	0.001
5	0.05	0.243	0.256	0.0404	0.0241	0.002	0.001
6	0.06	0.337	0.251	0.0439	0.0378	0.002	0.001
7	0.05	0.211	0.213	0.0677	0.0228	0.001	nil
8	0.05	0.296	0.251	0.0600	0.0205	0.003	0.001
9	0.07	0.264	0.195	0.0669	0.0350	0.002	0.001
10	0.06	0.256	0.211	0.0579	0.0329	0.002	0.001
11	0.09	0.224	0.211	0.0617	0.0270	0.003	0.001
12	0.09	0.283	0.208	0.0795	0.0546	0.001	0.002
13	0.08	0.269	0.184	0.0511	0.0368	0.002	0.001
14	0.06	0.342	0.220	0.0646	0.0229	0.001	0.001
15	0.05	0.323	0.288	0.0603	0.0298	0.002	0.001
Average.....	0.07	0.282	0.225	0.0534	0.0306	0.002	0.001

The elimination of FeO is likewise an inherent part of the steelmaking process. In rimming steel a reduction of FeO occurs in the ladle. The major elimination occurs, however, as a result of the C-FeO reaction and the rimming action in the ingot mold. A loss of 0.02 per cent carbon between the ladle and the finished steel is not unusual. Such a reduction in carbon is equivalent to 0.12 per cent FeO (C:FeO::12:72). In killed and semikilled steel the amount and composition of the oxides in the finished product are governed by the degree of oxidation of the bath, the amount, type, and sequence of deoxidizers, temperature and the type of mold used.

*Oxides in Low-carbon Steel at Tapping, at Pouring, in Test-mold Samples and in Finished Steel.*—Aluminum-killed samples offer the only available means for determining the oxygen content of the bath. The precise distribution of the total oxygen thus determined is not known. It may exist as FeO, CO, MnO, and  $\text{SiO}_2$ . It is generally assumed,

however, that the major portion exists as FeO. Fig. 20 and Table 6 illustrate a number of general relations pertinent to the problem of oxides in low-carbon steel. The carbon content of a series of 15 heats is given

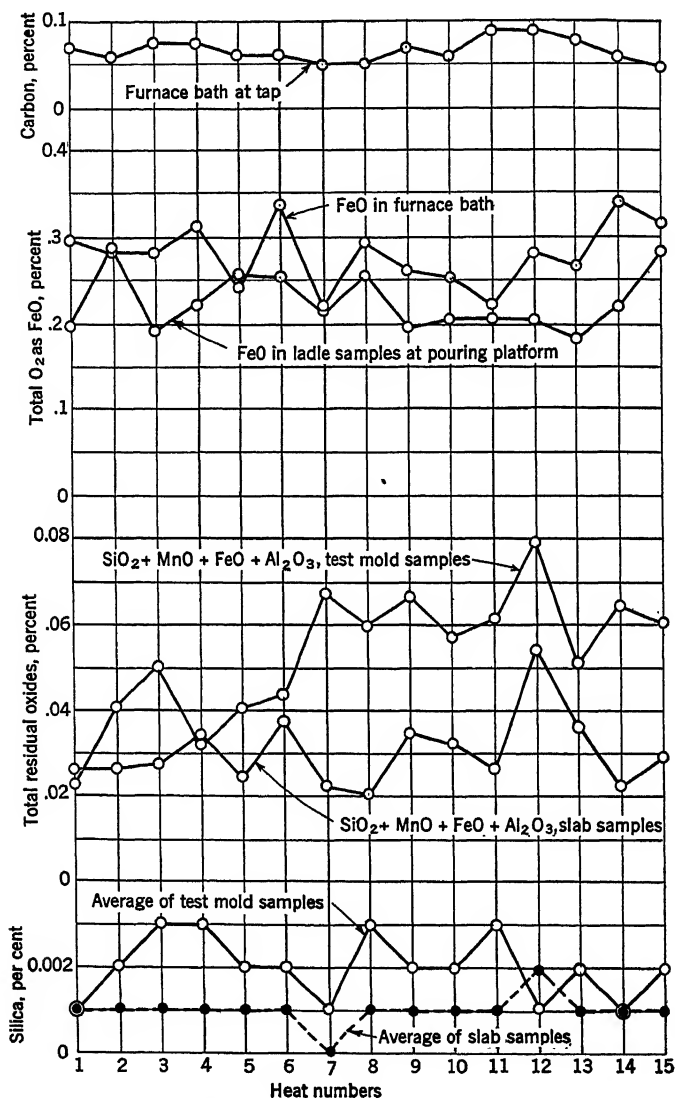


FIG. 20.—OXIDES IN LOW-CARBON STEEL AT TAPPING, AT POURING, IN TEST-MOLD SAMPLES AND IN SLABS.

at top of Fig. 20. The two adjacent curves show the total oxygen as FeO in the bath and at the pouring platform. All heats except three show a substantial reduction of FeO between the furnace bath and the steel in the ladle at the pouring platform. It is likely that the FeO in

these three heats may have been higher than the amount indicated by the killed samples, owing to an unavoidable delay in tapping.

The next pair of curves gives the total residual oxides ( $\text{FeO}$ ,  $\text{MnO}$ ,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ) in test-mold samples and samples from the middle of two test ingots. There is no fixed relation between the  $\text{FeO}$  in the bath and the residual oxides in test-mold samples or in the slab samples. The curves do show, however, that only a minor part of the total oxygen as  $\text{FeO}$  in the bath is retained in the finished steel. The slab samples were lower in residual oxides than rimmed samples taken at the pouring platform. Although a large part of the  $\text{FeO}$  in liquid steel is eliminated during the rimming action in a test mold, the elimination is more thorough in the ingot mold. Cropping of the ingot also tends toward a product more nearly free from inclusions. While test-mold samples are not entirely satisfactory, normally they indicate the relative cleanliness of the finished steel.

The curves at the bottom of Fig. 20 show that only small amounts of  $\text{SiO}_2$  (0.002 to 0.003 per cent) will exist in the bath in the presence of 0.2 to 0.3 per cent  $\text{FeO}$ . Any  $\text{SiO}_2$  as such, or as silicates in the iron, does not persist in the open-hearth bath in the presence of  $\text{FeO}$  introduced to eliminate carbon. In general slab samples were lower in  $\text{SiO}_2$  than test-mold samples. The  $\text{SiO}_2$  in test-mold samples from the 15 heats averaged 0.002 per cent  $\text{SiO}_2$ , compared to 0.001 per cent for slab samples. (See average results, Table 6.)

With an average of 0.07 per cent carbon the total oxygen as  $\text{FeO}$  averaged 0.282 per cent for the 15 heats. Between the bath and the pouring platform the  $\text{FeO}$  decreased from 0.282 to 0.225 per cent. The total residual oxides in test-mold samples averaged 0.053 per cent, or about 20 per cent of the  $\text{FeO}$  in the bath before tap. Residual oxides in slab samples averaged 0.031 per cent, or about 10 per cent of the  $\text{FeO}$  in the furnace bath just before tapping. The  $\text{SiO}_2$  in test-mold samples and in slab samples is insignificant when compared with the amount of  $\text{FeO}$  in low-carbon steel at tapping. In short, the question of oxides in low-carbon steel consists primarily of the introduction of  $\text{FeO}$  to eliminate carbon and the subsequent removal of this  $\text{FeO}$ .

If the amount of oxides in pig iron is to be related to the amount in the steel, the comparison should be made between the oxides in the iron and in the bath before deoxidation. Test-mold samples of iron retain substantially all the oxides in the liquid iron, whereas test-mold samples of steel retain only a portion of the oxides (largely  $\text{FeO}$ ) in the liquid steel. For this reason all bath samples in this investigation were taken in pairs—a killed sample and a rimmed sample.

*Open-hearth Tests.*—Specific data on the oxides in basic iron and open-hearth steel were obtained from 23 heats. Samples of the iron were taken from transfer ladles. Most of the iron came from the mixer but some



direct metal was used. The first pair of bath samples, one killed and the other wild, was taken when all the scrap had melted. In most heats at least three additional pairs of samples were taken before tapping. Average data on several hundred casts of iron show that about two-thirds of the total oxides is FeO. It has been shown, however, that the FeO in the open-hearth bath, up to the point where deoxidizers are added, is largely a function of the carbon (Fig. 19). The effect of FeO in the pig iron on the oxides in the steel can therefore be neglected. A study of 51 heats of low-carbon steel gave some indication that less ore was used during periods when the iron was high in FeO. If other factors, such as the type of scrap charge, remain about the same, the FeO in the iron may affect the amount of carbon in the bath at melt-down.

A comparison between the  $\text{SiO}_2$  in the iron and in the steel bath before deoxidation will show the degree to which  $\text{SiO}_2$  as such or as silicates persists through the open-hearth process. Figs. 21 and 22 show the  $\text{SiO}_2$  in the iron and in the bath from melt-down to tap for eight typical heats. If the iron contained substantial amounts of  $\text{SiO}_2$ , most of it was eliminated before the first bath test was taken. During the working and finishing periods the  $\text{SiO}_2$  in the bath ranged from 0.001 to 0.003 per cent. If the iron was unusually low in  $\text{SiO}_2$ , bath samples showed an increase. (See heat 23, Fig. 22.) The molten iron charged into 21 heats averaged 0.008 per cent  $\text{SiO}_2$ , compared to an average of 0.002 per cent in the bath before the addition of deoxidizers.

It is clear from the curves in Figs. 21 and 22 that any  $\text{SiO}_2$  as such or as silicates is reduced to very small amounts when the carbon is still comparatively high and the FeO comparatively low. The elimination of  $\text{SiO}_2$  or silicates was probably simultaneous with the elimination of some 2 per cent manganese and 1 per cent silicon early in the heat. Large amounts of  $\text{SiO}_2$  and  $\text{MnO}$ , formed by oxidation of manganese and silicon, should and do apparently exert a favorable fluxing action on any  $\text{SiO}_2$  or silicates in the iron.

Heats 20, 21 and 23 (Fig. 22) are of special interest, as they illustrate the effect of silicon additions upon the  $\text{SiO}_2$  in the bath. In heat 20 the  $\text{SiO}_2$  increased from 0.003 to 0.01 per cent following an addition of ferro-silicon (15 per cent). The  $\text{SiO}_2$  in the bath in heat 21 increased from 0.0015 to 0.009 per cent following a similar addition of silicon to the bath. By the time the ladle reached the pouring platform, the  $\text{SiO}_2$  had dropped to 0.0028 per cent as a result of ladle additions and the elimination of silicates. The  $\text{SiO}_2$  in the bath increased during the latter part of heat 23 to 0.007 per cent, then dropped to 0.0053 per cent 25 min. before tap. The increase in  $\text{SiO}_2$  in the ladle sample reflects the effect of an addition of silicon to the ladle. These heats illustrate the well-known effect of additions of deoxidizers upon the amount and composition of inclusions in the finished steel.

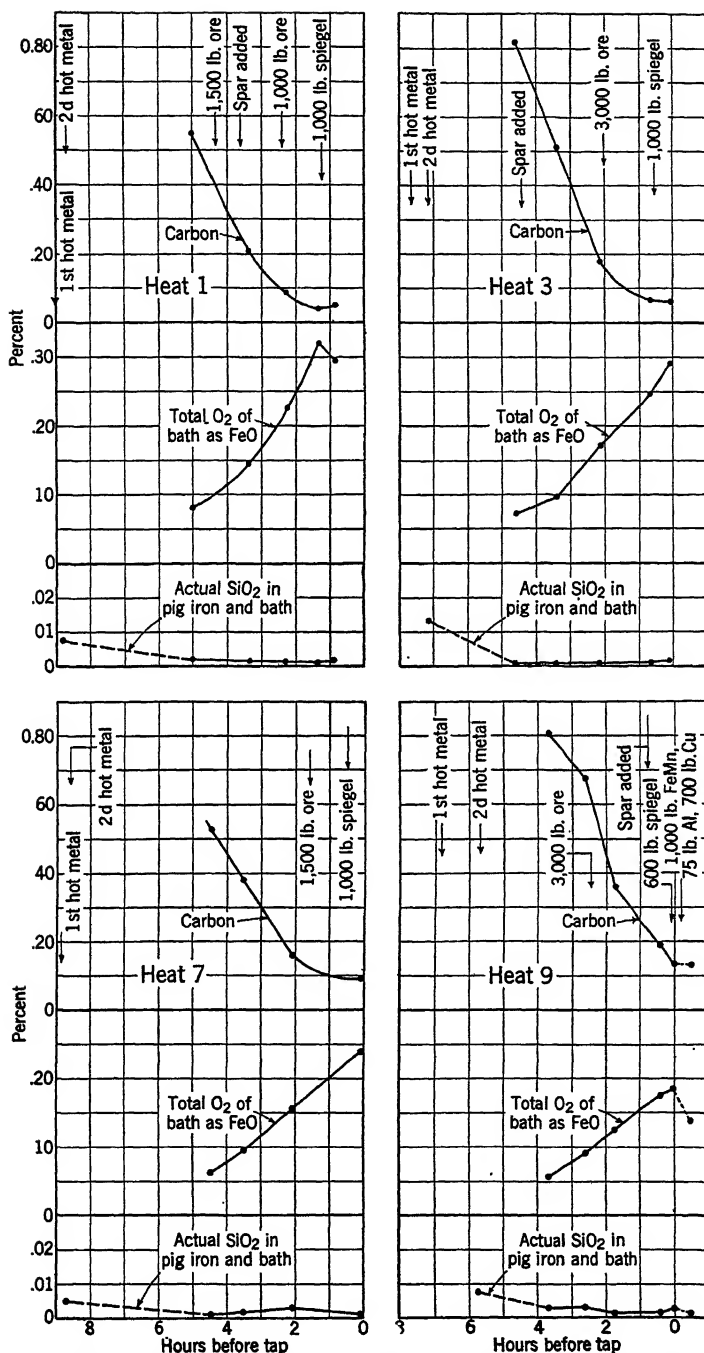


FIG. 21.—ACTUAL SILICA IN THE PIG IRON AND IN THE BASIC OPEN-HEARTH BATH (HEATS 1, 3, 7, AND 9).

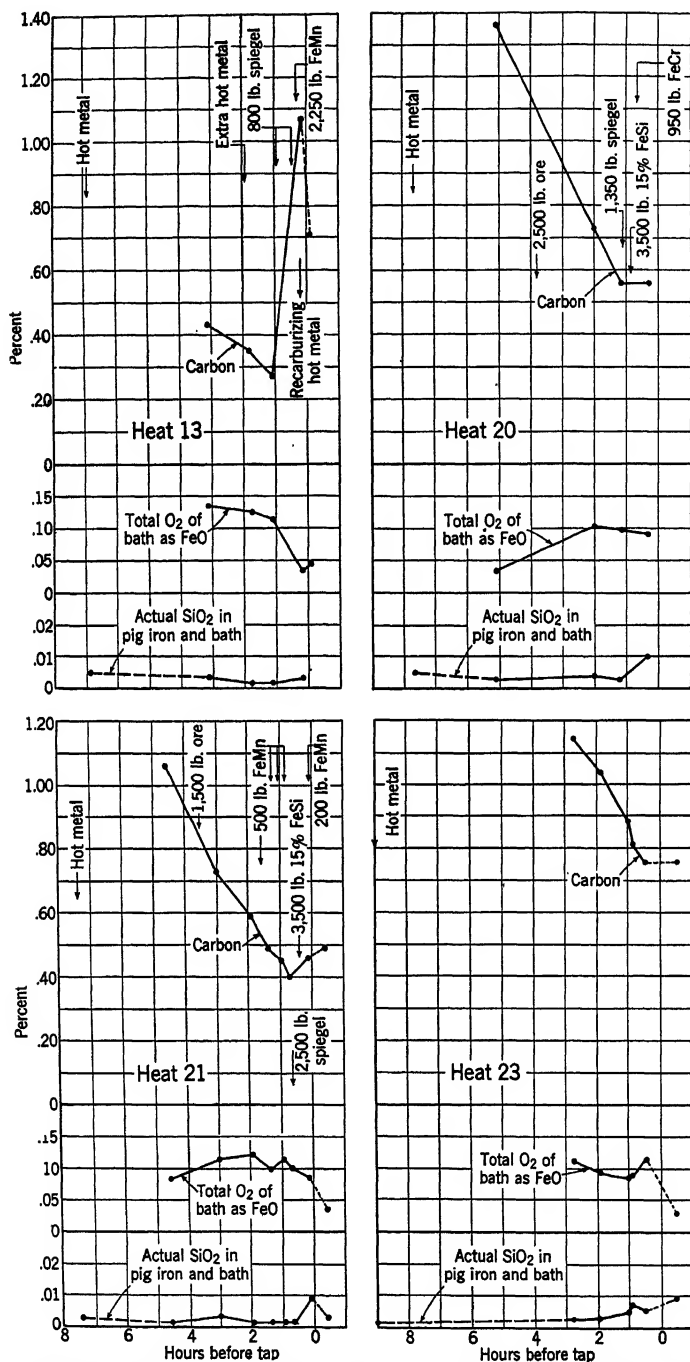


FIG. 22.—ACTUAL SILICA IN THE PIG IRON AND IN THE BASIC OPEN-HEARTH BATH (HEATS 13, 20, 21, AND 23).

*Summary of Oxides in Iron Charge and in Furnace Bath before Deoxidation.*—Information has been presented as to the carbon, total oxygen as FeO, and the  $\text{SiO}_2$  in the bath at various stages of eight heats. Detailed

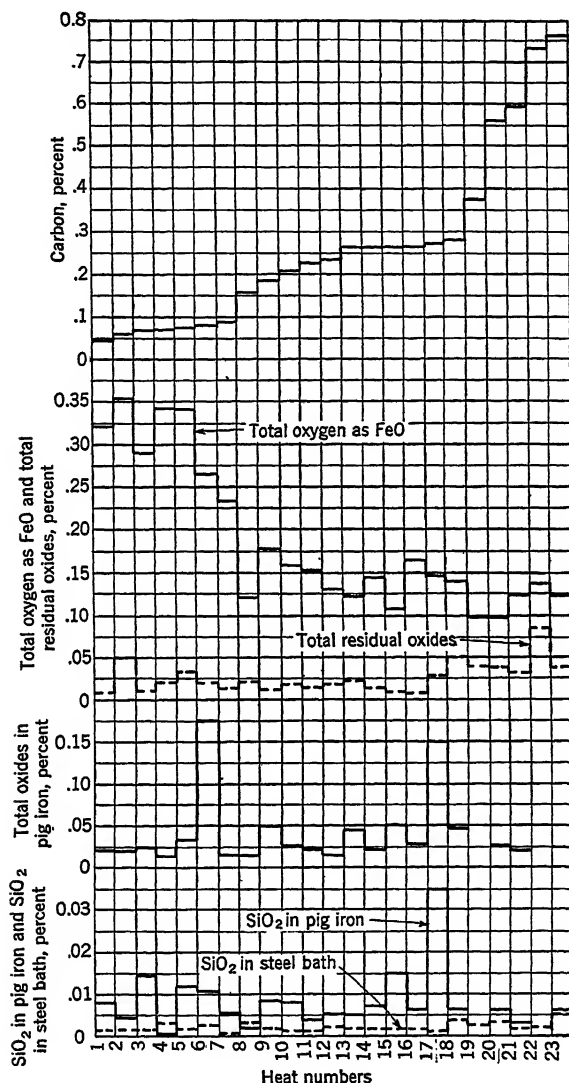


FIG. 23.—OXIDES IN BASIC PIG IRON AND IN THE OPEN-HEARTH BATH BEFORE DEOXIDATION.

data on 15 other heats duplicate the results given for the eight heats so closely that only a summary of oxides in the bath before the addition of deoxidizers will be given for all heats. This summary is given in Fig. 23. The heats are arranged in order of increasing carbon content. As the

carbon increases the FeO decreases in accordance with the general relation shown in Fig. 19. For carbon content up to about 0.25 per cent the total amount of residual oxides (FeO, MnO, SiO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub>) is very small compared with the total oxygen as FeO. This is particularly true for the first eight heats, which contain less than 0.10 per cent carbon. Above 0.25 per cent carbon a much higher proportion of the total oxygen as FeO was retained in the unskilled samples.

The bottom of Fig. 23 shows the total oxides in the iron, the SiO<sub>2</sub> in the iron and in the bath before deoxidation. In most cases the SiO<sub>2</sub> in the iron was higher than in the bath. There is no indication, however, that the amount of SiO<sub>2</sub> in the bath before deoxidation is in any way related to the amount in the iron. The bath in heats 4 and 8 contained more SiO<sub>2</sub> than the iron charge. Heats charged with iron highest in oxides showed no tendency for the bath to contain more SiO<sub>2</sub> (see heats 3, 15, 17).

#### OXIDES IN IRON AT THE BLAST FURNACE AND AT THE OPEN HEARTH

No special study was made to determine the change that took place in the oxides in the iron between the blast furnace and the open hearth. The analyses given in Table 7 represent a considerable tonnage of iron held in the mixer at the time hot metal was taken for the 23 heats of steel. It appears that some elimination of oxides occurs between the blast furnace and the open hearth. A comparison between the oxides in 194 casts sampled at the blast furnace and the iron used in 23 heats is given in Table 8. The composition of the oxide residue is about the same, but the comparison indicates a loss of oxides between the blast furnace and the open hearth.

*Temperature of Direct Metal and Metal from Mixer.*—The temperature of the iron was taken with an optical pyrometer as it was poured into the open hearth. Conditions were favorable for accurate readings. The results are given in Table 9. The temperature of direct metal averaged 147° F. above the temperature of mixer metal. From the curve in Fig. 5, giving the relation between temperature of the iron and the percentage of silicon and sulphur present, it is possible to estimate the average temperature at the blast furnace. Samples of iron from transfer ladles at the open hearth averaged 1.06 per cent silicon and 0.028 per cent sulphur (Table 10). The average temperature in the blast-furnace runner of iron of this analysis is estimated at 2610° F. Iron from the mixer averaged 2435° F., or 175° below the average temperature in the blast-furnace runner.

The temperature of the iron used for individual heats of steel varies widely, depending on whether it is direct or mixer metal. Observations on mixer metal ranged from 2346° to 2500° F. This variation is attributed to the amount of metal in the mixer and the lapse of time since a fresh

metal charge was received from the blast furnace. Fitterer<sup>7</sup> observed that the depletion of metal in the mixer resulted in a gradual drop in the temperature of the iron in the mixer. In extreme cases the temperature decreased 135° F. He also observed that the temperature of molten iron

TABLE 7.—*Oxides in Samples of Molten Iron from Transfer Ladles at the Open Hearth*

Iron Used in Heat No.	Oxides in Sample, Per Cent				Total Oxides, Per Cent	Composition of Residue, Per Cent			
	SiO <sub>2</sub>	MnO	FeO	Al <sub>2</sub> O <sub>3</sub>		SiO <sub>2</sub>	MnO	FeO	Al <sub>2</sub> O <sub>3</sub>
1	0.0075	0.0048	0.0059	nil	0.0182	41.2	26.4	32.4	
2	0.0039	0.0026	0.0088	0.0018	0.0166	20.2	13.5	57.8	8.8
3	0.0138	0.0020	0.0091	nil	0.0249	55.4	8.1	36.5	
4	tr.	0.0013	0.0100	0.0022	0.0136	0.7	9.6	73.5	16.2
5	0.0115	0.0031	0.0166	nil	0.0310	36.8	10.0	53.0	
6	0.0107	0.0011	0.1611	nil	0.1729	6.4	0.6	93.0	
7	0.0050	0.0018	0.0046	nil	0.0114	43.8	15.8	40.4	
8	0.0007	0.0024	0.0085	nil	0.0116	6.0	20.8	73.2	
9	0.0073	0.0103	0.0281	nil	0.0457	16.0	22.6	61.4	
10	0.007	0.0045	0.0077	nil	0.0192	36.8	23.2	40.0	
11	0.0034	0.0026	0.0088	0.0018	0.0166	20.4	15.6	53.2	10.8
12	0.0053	0.0029	0.0051	nil	0.0133	39.8	21.8	38.4	
13	0.0051	0.0034	0.0313	nil	0.0398	12.8	8.6	78.6	
14	0.0073	0.0025	0.0075	nil	0.0173	42.2	14.5	43.3	
15	0.0158	0.0066	0.0224	nil	0.0448	35.2	14.8	50.0	
16	0.0065	0.0053	0.0119	nil	0.0237	27.4	22.2	50.4	
17	0.0353	0.0051	0.1029	0.0042	0.1475	24.1	3.4	69.6	2.9
18	0.0060	0.0053	0.0292	nil	0.0405	14.8	13.1	72.1	
20	0.0051	0.0035	0.0105	nil	0.0191	26.7	18.3	55.0	
21	0.0026	0.0019	0.0074	0.0016	0.0135	19.3	14.1	54.7	11.9
23	0.0006	0.0028	0.0162	nil	0.0196	3.1	14.3	82.6	
Average.....	0.0076	0.0036	0.0245	0.0005	0.0362	21.0	10.0	67.6	1.4

TABLE 8.—*Oxides in 194 Casts at Blast Furnace and Iron Used in 23 Heats*

	Oxides in Sample, Per Cent				Total Oxides	Composition of Residue, Per Cent			
	SiO <sub>2</sub>	MnO	FeO	Al <sub>2</sub> O <sub>3</sub>		SiO <sub>2</sub>	MnO	FeO	Al <sub>2</sub> O <sub>3</sub>
Blast furnace.....	0.011	0.007	0.032		0.050	22.0	14.0	64.0	
Open hearth.....	0.008	0.0036	0.0245	0.0005	0.032	21.0	10.0	67.6	1.4

moved from the blast furnace to the mixer in submarine ladles decreased more rapidly if the ladle lining was comparatively cold. If the iron as tapped from the blast furnace is uniformly high and the method of handling is the same, it will reach the open hearth at higher temperatures.

It is evident, however, that the temperature of the iron at the open hearth will vary widely, depending upon the manner in which it is handled after it leaves the blast furnace.

*Analysis of Iron Reported to Open-hearth Melter and Analysis of Samples from Transfer Ladles.*—The analysis of iron in the mixer was computed from the weights and analyses of the last five casts received from the blast furnace. An analysis thus computed was reported to the open-hearth

TABLE 9.—*Temperature of Direct Metal and Metal from Mixer as Poured into the Open Hearth*

TEMPERATURES TAKEN WITH OPTICAL PYROMETER

Direct Metal, Temperature, Deg. F.	Mixer Metal, Temperature, Deg. F.		
2,632	2,412	2,445	2,468
2,588	2,459	2,500	2,442
2,553	2,463	2,390	2,451
2,543	2,441	2,456	2,360
2,612	2,390	2,484	2,346
2,570	2,360	2,478	2,458
2,605	2,390	2,385	2,462
2,543	2,390	2,390	2,485
2,595	2,468	2,390	2,478
Average 2,582			2,435

melter when hot metal was obtained from the mixer. When the metal came directly from the blast furnace, the cast analysis was reported to the open hearth. Table 10 gives a group of analyses as reported to the open-hearth melter and the analysis of corresponding transfer-ladle samples. With one exception the reported and ladle analyses agree fairly well. The difference, in silicon, between the two corresponding analyses averaged 0.06 per cent. The average analysis, as reported to the open-hearth melter, is very close to the average analysis of ladle samples (Table 10). No evidence of stratification in the mixer was obtained. This may be due to the fact that the iron was fairly uniform in composition and well sampled at the blast furnace. Casts from the blast furnace were sampled under the supervision of the laboratory according to volume as determined by the filling of successive ladles.

#### SUMMARY AND CONCLUSIONS

The temperature of several hundred casts of metal produced in a 700-ton furnace operating on Lake ores was measured with noble-metal thermocouples to observe the effect of temperature upon the oxides in the iron. A definite relation between silicon and sulphur was established, but no relation was found between the oxides in the iron and the tempera-

TABLE 10.—*Analysis of Iron Reported to Open-hearth Melter and Analysis of Samples from Transfer Ladles<sup>a</sup>*

Analysis Reported to Open-hearth Melter, Per Cent				Analysis of Ladle Samples, Per Cent			
Silicon	Sulphur	Manganese	Phosphorus	Silicon	Sulphur	Manganese	Phosphorus
1.10	0.026	1.97	0.198	0.98	0.024	1.92	0.221
1.07	0.027	1.78	0.208	1.07	0.028	1.78	0.234
1.13	0.024	1.76	0.232	1.06	0.024	1.77	0.232
1.07	0.027	1.78	0.208	1.06	0.025	1.80	0.227
0.99	0.034	1.68	0.190	0.94	0.038	1.70	0.217
1.15	0.029	1.95	0.175	1.21	0.027	1.85	0.205
1.15	0.029	1.95	0.175	1.22	0.027	1.85	0.205
1.15	0.029	1.95	0.175	1.21	0.027	1.87	0.202
0.70	0.032	1.52	0.170	0.68	0.036	1.57	0.192
1.05	0.028	1.79	0.182	0.93	0.030	1.86	0.202
1.05	0.025	1.93	0.235	0.94	0.024	1.89	0.250
1.05	0.025	1.93	0.235	0.93	0.025	1.96	0.253
1.08	0.025	1.92	0.184	0.96	0.024	1.91	0.192
1.08	0.025	1.92	0.184	0.97	0.024	1.92	0.197
1.14	0.025	1.90	0.162	1.32	0.030	1.68	0.162
1.15	0.027	1.92	0.187	1.20	0.030	1.84	0.192
1.15	0.027	1.92	0.187	1.22	0.027	1.87	0.207
1.15	0.027	1.92	0.187	1.23	0.027	1.88	0.210
1.14	0.026	1.94	0.218	1.10	0.030	1.89	0.212
1.14	0.026	1.94	0.218	1.07	0.030	1.90	0.212
1.16	0.026	2.01	0.161	1.09	0.030	1.86	0.192
1.16	0.026	2.01	0.161	1.10	0.029	1.84	0.187
1.05	0.028	1.87	0.203	1.06	0.030	1.85	0.212
1.05	0.028	1.87	0.203	1.07	0.030	1.83	0.210
0.86	0.031	1.80	0.150	0.86	0.030	1.69	0.185
1.07	0.029	1.87	0.158	0.99	0.028	1.85	0.192
1.00	0.030	1.54	0.165	0.98	0.028	1.69	0.192
0.99	0.031	1.83	0.158	0.98	0.029	1.82	0.192
1.14	0.025	1.97	0.183	1.15	0.027	1.84	0.195
1.14	0.025	1.97	0.183	1.16	0.028	1.81	0.202
1.16	0.026	2.01	0.161	1.05	0.029	1.97	0.200
1.16	0.026	2.01	0.161	1.07	0.030	1.88	0.197
1.25	0.027	1.94	0.196	1.22	0.031	1.85	0.225
1.07	0.029	1.87	0.158	1.01	0.028	1.84	0.190
1.07	0.029	1.87	0.158	1.00	0.028	1.85	0.192
1.09	0.027	1.88	0.185	1.06	0.028	1.83	0.205

<sup>a</sup> Average difference in silicon between reported analysis and ladle analysis equals 0.06 per cent.

ture of the iron. Close control of the silicon and sulphur in the iron requires that the average temperature of the iron be held within narrow limits. In general, a variation of 40° F. in the average temperature of the iron in the runner will result in a 10-point (0.10 per cent) variation in



silicon and a 2-point (0.002 per cent) variation in sulphur. Variations in sulphur, silicon and temperature are due largely to variations in the pattern of gas distribution in the furnace shaft. Uniform gas distribution requires careful control of the size of materials and distribution of stock.

The total oxides in the iron ranged from 0.012 to 0.313 per cent. As the total oxides increased the percentage of FeO in the oxide residue increased. The oxide residues from 194 casts averaged 22 per cent  $\text{SiO}_2$ , 14 per cent MnO and 64 per cent FeO. A small amount of  $\text{Al}_2\text{O}_3$  was found in occasional casts.

Microscopic examinations at 50 diameters disclosed the presence of large inclusions in some samples. Small, irregular inclusions observed at 1000 diameters were more characteristic of the samples studied. No definite relation was found between the number or size of inclusions and the amount of oxides as determined by electrolytic extraction. Some tendency was shown for the inclusions to be associated with the graphite. The oxide content of the iron had no apparent effect on the form of the graphite.

The cause for variations of the oxides in the iron was not determined. Groups of casts low in total oxides (0.019 per cent) contained practically the same amount of silicon and sulphur as groups of casts high in total oxides (0.1 to 3.0 per cent). Casts extremely high in oxides showed the greatest variation in silicon from the previous cast. In the low and intermediate range of oxides the variation in silicon was about constant. No consistent relation was found between furnace practice and the oxides in the iron.

A relation established between the carbon and total oxygen in 150 aluminum-killed samples shows that the FeO in the bath before deoxidation is primarily a function of the carbon in the bath. Variations in the ferrous oxide in the iron have no effect upon the iron oxide in the open-hearth bath. Any tendency for finely dispersed  $\text{SiO}_2$  or silicates in the iron to persist through the open-hearth process can be detected from  $\text{SiO}_2$  determinations on the iron and the open-hearth bath. The amount of  $\text{SiO}_2$  in the bath of 23 heats of steel before deoxidation showed no relation to the amount of  $\text{SiO}_2$  in the molten iron charge.  $\text{SiO}_2$  as such or in combination in the form of silicates is largely eliminated early in the heat, when large amounts of  $\text{SiO}_2$  and MnO are formed adjacent to inclusions in the iron.

In rimming steel the FeO introduced into the bath to eliminate carbon is largely eliminated by the C-FeO reaction and the rimming action in the ingot mold. In killed or semikilled steel this FeO is reduced to metallic iron by deoxidizers. The cleanliness of the steel depends upon the amount of FeO present and the degree to which the products of deoxidation are eliminated. The introduction of FeO into the steel bath and its subsequent elimination are basic features of an oxidizing process.

The temperature of molten-iron charge for individual heats varies, depending upon the manner in which the iron is handled after it leaves the blast furnace. Metal moved to the open hearth in submarine ladles and transfer ladles is substantially higher in temperature than metal from a hot metal mixer. Variations in temperature of the iron at the open hearth, due to differences in methods of handling the iron after it leaves the blast furnace, are greater than the variations in the temperature of individual casts in uniform blast-furnace practice.

The analyses of metal reported to the open-hearth melter were approximately the same as the analyses obtained from samples taken from transfer ladles. Differences between the reported and actual analysis of the iron depend upon the uniformity of the iron and the method of sampling at the blast furnace. There was no evidence of stratification in the mixer. Data from this investigation do not, however, preclude the possibility of stratification when the iron varies widely in analysis.

#### ACKNOWLEDGMENTS

This investigation, which was initiated by officials of the Inland Steel Co., was conducted by the U. S. Bureau of Mines in cooperation with the Inland Steel Co., and the work was done at the company's plant at Indiana Harbor, Ind. The author wishes to acknowledge the support and interest of officials of the company, who fully cooperated with the Bureau of Mines in this investigation. These include J. H. Walsh, Works Manager; H. R. deHoll, General Superintendent; J. H. Nead, Chief Metallurgist; H. W. Johnson, Blast-furnace Superintendent; and H. B. Hubbard, Open-hearth Superintendent.

Grateful acknowledgment is made to F. W. Scott, Chemist, for his general assistance and in particular for determining the oxides in samples of pig iron and steel by his electrolytic method. W. M. Douglas rendered valuable aid in obtaining continuous records of the temperature of the iron in the blast-furnace runner. Microscopic examinations of pig-iron samples for oxides were made by J. F. Woschitz and J. W. Halley. Slag and metal samples were analyzed under the supervision of C. O. Geyer, Chief Chemist.

#### APPENDIX

*Extraction and Analysis of Oxides from Pig Iron.*—This method of oxide extraction has been published in detail<sup>8</sup>, but subsequent work on hundreds of samples has led to a number of small changes and modifications that make it desirable to review the procedure briefly.

*Extraction Cell.*—The construction of the cell, shown diagrammatically in Fig. 24, is simple and inexpensive. The cell consists of a large-mouthed 3-liter bottle lined with a copper screen cathode. Suspended in the center of the bottle is a glass tube. A hardened filter paper, which

acts as a membrane, is fastened across the bottom of the glass tube. A small reagent bottle with bottom removed has been found convenient for use as the inner cell. The sample of iron is suspended in the inner cell by means of a platinum wire, and is the anode.

*The Electrolyte.*—The electrolyte is a 5 per cent solution of magnesium iodide in which approximately 5 grams of iodine has been dissolved. This may be prepared by allowing 120 grams of iodine to react with magnesium metal until magnesium hydroxide appears and then filtering

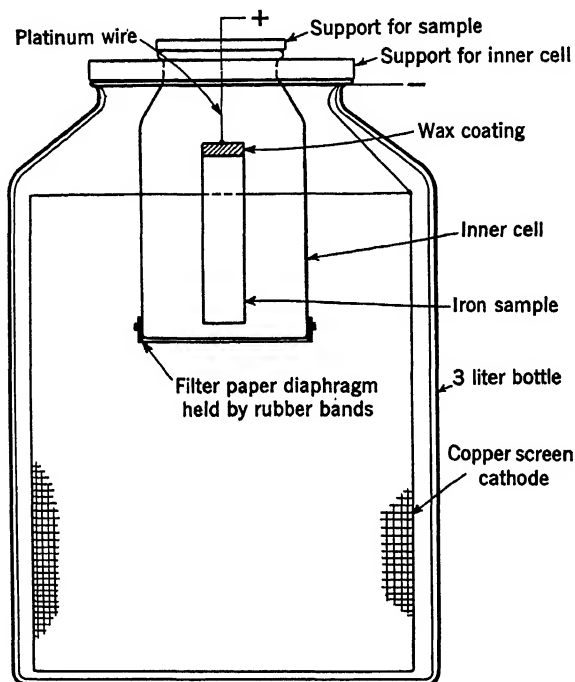


FIG. 24.—DIAGRAMMATIC SKETCH OF CELL USED IN ELECTROLYTIC EXTRACTION METHOD.

the solution. Dissolve 5 grams of iodine in the filtered solution and dilute to volume.

*Source of Power.*—The source of power is an ordinary heavy-duty storage battery equipped with a charger. In this investigation 10 cells were operated simultaneously using 10 amp. per hour, which required that the charger supply the 10 amp. It should be so arranged that the charging rate can be varied according to the demand. Each extraction cell should have a variable resistance in the circuit so that the amperage can be controlled at 1 amp. At this rate about one gram of iron or steel will be decomposed each hour.

*Preparation of Sample.*—It is desirable to extract a sample of at least 50 grams and up to 100 grams. More than this weight of sample causes

the graphite and carbon to be so voluminous that filtering and washing are difficult. The extraction is aided by having a sample of large area for its weight. In this work the pieces of pig iron were about 4 in. long, 1 in. wide and  $\frac{1}{8}$  in. thick. After the samples are cut from the casting the edges are filed and the sample is cleaned of all oil, grease and dirt, and then weighed. A platinum wire is attached to the sample and the upper portion, which will not be submerged in the electrolyte, must be waxed. The sample is then suspended in the inner cell and the electrolysis proceeds.

*Electrolysis.*—At first the electrolysis will proceed rapidly, but as the area of the metal is reduced more voltage must be impressed to maintain the one ampere. Soon it will not be possible to keep so much amperage on the cell, but the electrolysis should proceed until the ammeter shows that all action has ceased. It is then ready to remove. The iron sample will retain its original shape and usually clings to the wire. It will be black and have a coating of iodine on the outside.

*Washing and Treatment of Residue.*—Remove the sample from the jar by lifting out the platinum wire to which it is attached. Place in a casserole and gently remove the decomposed portion. If there is a core of undecomposed iron, scrape it clean with a spatula. Clean the stub and weigh. The weight of the sample is the difference between the weight when introduced into the cell and the weight of the stub.

An inspection of the carbon skeleton will tell whether any has fallen off into the inner cell. If this has happened, filter the solution of the inner cell and add the recovered portion of the residue to that in the casserole.

In the extraction of pig iron a considerable amount of iodine is plated out on the carbon skeleton. This, along with the ferrous iodide, magnesium iodide, and the silicic acid, must be removed by suitable washing. Any small particles of metallic iron also must be removed. The following scheme was adhered to in this investigation.

Moisten the residue in the casserole with a solution of 15 grams potassium iodide and 15 grams ammonium citrate in 50 ml. of water, then grind in a casserole with an agate pestle until all the carbon is very finely divided and the solution is a smooth slurry. This is very important, as the carbon has absorbed such a large amount of salts that a thorough washing can be accomplished only if there are no lumps. During the grinding the solution may be decanted into an 800-ml. beaker; the larger pieces remain in the casserole and are then ground. Often during this operation and decantation the oxides may be seen in the casserole and their types observed. When the grinding is complete transfer all the residue to the beaker and dilute to 600 ml. Allow it to stand for 24 to 48 hours. Then filter the solution on a suction filter by means of a 45-mm., very retentive, ashless filter paper. In this work a special device, similar to a carbon tube, was developed because a number of filtrations are required on each sample and the bulk of the filter-pape

pulp hampers the washing of the residue. After filtration, wash the residue thoroughly with cold water.

Return the washed residue to the beaker and add 100 ml. of solution containing 10 grams of potassium iodide and 20 grams of sodium citrate. Agitate several times during the day and dilute to 600 ml. in the evening. Allow the solution to stand overnight, then filter and wash with cold water. Repeat this treatment at least three times, or until all trace of color disappears from the solution after it has stood overnight. After the last filtration place the residue in the beaker, to which 50 ml. of copper sulphate solution has been added (250 grams of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  to liter of solution, with 1 gram  $\text{MgO}$  and 2 grams  $\text{MnCO}_3$  added). Filter the solution as it is used. Agitate the residue several times during the day and dilute to 400 ml. in the evening.

The next morning filter the sample and wash it with cold water. Then place the residue in the beaker with 400 ml. of solution containing 15 grams of ammonium citrate. Warm about 30 min., until the residue coagulates and settles to the bottom of the beaker. Filter and wash with hot water. Return the residue to the beaker, and add 400 ml. of solution containing 30 grams of sodium hydroxide and 30 grams of sodium tartrate. Warm gently for about 30 min. or until the residue coagulates and settles out; then filter, and wash thoroughly with hot water. Return the residue to the beaker, add 400 ml. of water containing 10 grams of ammonium citrate, and warm again for about 30 min. Filter with suction, and wash until the washings are colorless. Suck dry, and place the residue and paper pulp in a platinum dish or crucible. Dry and ignite. The residue will contain  $\text{SiO}_2$ ,  $\text{Mn}_2\text{O}_4$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{TiO}_2$ , and perhaps some traces of  $\text{Cr}_2\text{O}_3$ .

*Analysis of Residue.*—As most chemists prefer certain methods of analysis those used in this investigation will be sketched briefly:

1. After fusion with sodium carbonate, the fusion was leached out in the hydrochloric acid solution and the  $\text{SiO}_2$  dehydrated in sulphuric acid. The  $\text{SiO}_2$  was determined by volatilization with hydrofluoric acid and the residue in the platinum crucible was fused with potassium bisulphate and added to the filtrate from the  $\text{SiO}_2$ .

2. The copper was removed as  $\text{CuS}$  and the filtrate containing the iron, manganese, aluminum and titanium was boiled down to 100 ml. and oxidized with a few crystals of ammonium persulphate.

3. The solution was aliquoted into two portions, of which one was used for the manganese determination and one for the iron and alumina determinations.

4. The manganese was determined by the usual arsenite titration after persulphate oxidation. The manganese was calculated to  $\text{MnO}$ .

5. The iron, manganese and titanium were separated from the aluminum by the usual alkali separation and the aluminum was determined<sup>9</sup> as  $\text{AlPO}_4$ . The aluminum was calculated to  $\text{Al}_2\text{O}_3$ .

6. The iron, manganese and titanium were dissolved from the filter paper with hydrochloric acid. Tartaric acid was added and the solution was heated and then saturated with  $H_2S$ . It was then made strongly ammoniacal and the iron was separated as  $FeS$ . Then it was washed. The  $FeS$  was dissolved with hydrochloric acid and the solution boiled free of  $H_2S$ . It was then oxidized and the iron determined by titration or colorimetrically, depending upon the amounts present. The iron was calculated to  $FeO$ .

*Extraction of Samples from Steel Bath and Their Analyses.*—The extraction of the steel samples is the same as for the pig iron. The test pieces in this investigation were conical. After the outside was cleaned of oxides the more solid tip of the cone was cut off, drilled, and tapped. The platinum wire was then attached to the sample by a bolt. The top of the specimen was given a protective coating of wax and the tip was submerged and electrolyzed.

After the steel was extracted the oxide and carbon residues were found on the membrane paper. The entire contents of the inner cell must be filtered and added to the residue clinging to the rest of the sample. In the high-carbon ranges the residue must be ground in the same manner as the pig iron; in the lower ranges it is not necessary.

The residue is washed in the same manner as the pig-iron residue, except that the caustic wash and the following wash are eliminated, as there is no silicic acid present. The residue is analyzed by the method used for the pig-iron residue, except that there is no titanium present and its separation from the iron is unnecessary.

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## DISCUSSION

(C. H. Herty, Jr., *presiding*)

J. CHIPMAN,\* Middletown, Ohio.—This paper contains several valuable contributions to our knowledge of blast-furnace practice in the production of hot metal for the open hearth. The author's admirable method for measuring temperatures has enabled him to determine with the utmost certainty the relationship between the temperature and composition of the metal, with respect to sulphur and silicon, when other factors are essentially constant. Similarly, he has shown clearly the effect of total acids upon the sulphur content of the metal.

His discussion of oxides in pig iron centers around the results obtained by the electrolytic method used by Scott with some success in determining oxides in steel. This is an entirely unproved method as far as pig iron is concerned, and the nature of the results is sufficient to cast considerable doubt upon its dependability. At Dr. Joseph's request, I determined the oxygen content of five specimens by the vacuum-fusion method. His results and mine are compared in Table 11. It is evident that one method or the other is entirely erroneous.

TABLE 11.—*Comparison of Joseph and Chipman Results*

Cast No.	Composition, Per Cent				Oxygen, Per Cent	
	SiO <sub>2</sub>	MnO	FeO	Al <sub>2</sub> O <sub>3</sub>	Calculated	Vacuum-fusion Oxygen
2432	0.0089	0.0038	0.0158	Nil	0.0092	0.003
2548	0.0188	0.0074	0.2169	Nil	0.060	0.002
2302	0.0312	0.0043	0.4133	Nil	0.1096	0.002
2299	0.0615	0.0044	0.7113	Nil	0.1922	0.006
2301	0.0694	0.0096	0.8950	Nil	0.2384	0.018

Dr. Joseph finds that "the amount of SiO<sub>2</sub> in the bath of 23 heats of steel before deoxidation showed no relation to the amount of SiO<sub>2</sub> in the molten iron charge" (p. 238). This will be a great disappointment to those who have attempted to place the blame for all open-hearth ailments upon "oxides in the pig iron." If the author's analyses are accepted, this pig iron certainly contained enough oxides to do whatever damage oxides might be capable of doing.

It is becoming increasingly evident that the quality of hot metal for use in the open hearth is determined by three primary considerations: (1) its ordinary chemical analysis; (2) its temperature; and (3) the regularity with which these two factors are reproduced from cast to cast.

T. L. JOSEPH.—The samples analyzed for oxides with the vacuum-fusion method by Dr. Chipman were also reduced with hydrogen by Mr. Larsen. Results with the hydrogen reduction method are ten to twenty times higher than those reported for vacuum fusion and agree more closely with those of the electrolytic method. For example, the calculated oxygen by vacuum fusion was 0.002 per cent, 0.047 by hydrogen reduction and 0.11 by electrolytic extraction. The percentage of total oxygen reported by Mr. Larsen on the five samples was: cast 2432, 0.010; cast 2548, 0.028; cast 2302, 0.047; cast 2299, 0.110; cast 2301, 0.131. These particular samples

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were unusually high in oxides. We made no attempt to remove material from blow-holes in solid strips submitted to electrolysis as it was in the samples as taken. It is difficult to believe that these samples contained only 0.002 to 0.006 per cent total oxygen. We feel that Dr. Chipman's results are low, although we may be too high. We are not willing to admit that we are as much in error as the results of the vacuum-fusion method indicate. Much of the disagreement is probably due to the irregular distribution of oxides. Further work on more homogenous samples is needed to get a comparison of the various methods.

C. H. HERTY, \* JR., Bethlehem, Pa.—All this means is that we have to be cooperative to have a method for the determination of oxygen in pig iron.

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\* Research Engineer, Bethlehem Steel Co.



## Cooperative Study of Methods for the Determination of Oxygen in Steel

BY J. G. THOMPSON,\* H. C. VACHER\* AND H. A. BRIGHT\*

(New York Meetings, February, 1936, and February, 1937)

THE methods employed for the determination of oxides and oxygen in ferrous materials may be roughly classed in two groups, "wet" methods and "hot" methods, the first group including the iodine, electrolytic, mercuric chloride, hydrochloric acid, nitric acid, and chlorine methods; the second group including the vacuum-fusion and hydrogen-reduction methods. The wet methods depend upon preferential solubility in a selected medium to separate the metallic portion of the sample from the oxygen-containing constituents. Subsequent analysis of the insoluble residue permits the isolation and separate determination of individual oxides and compounds. The hot methods depend upon the reduction of the oxide constituents of the sample by means of carbon or hydrogen at elevated temperatures. With the exception of the recently developed fractional vacuum-fusion method, the hot methods do not identify individual oxides and compounds but yield only a single value representing the sum of the oxygen contents of several or all of the oxide constituents present. With such diversity in the principles and aims of the different groups, it is not surprising that concordance of results by different methods has usually been difficult to obtain.

The present cooperative attempt to define more rigorously than has been possible heretofore the accuracy and limits of usefulness of the various methods, originated in correspondence between Dr. John Johnston, Director of Research of the United States Steel Corporation, and other interested metallurgists. The plan was, briefly, to submit identical samples to a number of laboratories for analysis by different methods and to collate the results of these analyses. The project was endorsed by the Iron and Steel Division of the American Institute of Mining and Metallurgical Engineers at the annual meeting in February, 1933, and has been conducted under the joint sponsorship of the Iron and Steel Division and the National Bureau of Standards. The latter organization undertook

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\* National Bureau of Standards of the U. S. Department of Commerce.

the preparation and distribution of sample material and the collection of data from the cooperating laboratories. The preliminary stages of the undertaking, described in progress reports<sup>1</sup> to the Iron and Steel Division, included the following items:

The study was limited to simple steels, i.e., plain carbon steels, to avoid complications introduced by the presence of alloying elements.

Seven plain carbon steels and one open-hearth iron were selected, covering a range in carbon, silicon, manganese, sulphur, phosphorus and oxygen contents. The selection was made chiefly from commercially available steels representing different melting and deoxidation practices to insure the presence in the different steels of different combinations and amounts of oxygen. Messrs. R. F. Mehl and C. H. Herty, Jr., procured the seven steels and the open-hearth iron recorded in Table 1, through the cooperation of the Jones and Laughlin Steel Corporation, the Carnegie Steel Company, and the American Rolling Mill Company.

For each of the eight compositions a portion of a single large ingot was selected, so as to obtain material as free as possible from vertical segregation. This section of the ingot, about 500 lb., was hot-rolled into rod approximately one inch in diameter. The material was converted into 1-in. rods to permit the use of a complete cross section of the rod, representing a complete cross section of the ingot, for the sample for each analysis. Difficulties in sampling, as a result of unavoidable variations in composition from skin to core, were thus avoided.

Each 500-lb. rod was divided into sections for convenience in handling, each section being marked to identify its relative position in the rod as rolled. The uniformity of the oxygen content along the length of each rod was established by vacuum-fusion analyses of samples taken at intervals throughout a length of rod sufficient to supply the desired amount of sample material. The maximum difference between the highest and lowest oxygen values for each of the seven steels was 0.003 per cent and for the open-hearth iron, with its higher oxygen content, the maximum difference was 0.01 per cent. These results indicated that the portion of each rod selected for sample material was satisfactorily uniform from end to end in oxygen content. Although some of the cooperating laboratories have ascribed their difficulty in obtaining check results, particularly in steel 3, to segregation of oxygen in the samples, there are no grounds for belief that there is enough segregation of oxygen to account for the discrepancies in results obtained by different cooperators using the same method of analysis.

Further study of possible segregation, both longitudinal and transverse in the rods, was made as follows: Transverse sections at intervals along the length of the selected portion of each rod were roughly polished

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<sup>1</sup> *Mining and Metallurgy* (1934) 15, 215; (1935) 16, 184.

TABLE 1.—*Type and Composition of the Selected Steels*

No.	Type	Additions			Composition, Per Cent						
		Furnace	Ladle	Mold	C	Si	Mn	S	P	Cr	V
1	Low-carbon, rimming.....	None	FeMn	None	0.03	0.002	0.31	0.036	0.011	0.004	<0.001
2	Medium-carbon, high-manganese, silicon-killed.....	FeMn	Hot metal, FeMn, FeSi	None	0.42	0.26	1.15	0.025	0.020	0.022	<0.001
3	Bessemer screw stock, rimming.....	None	FeMn, FeSi	FeSi	0.12	0.024	0.72	0.168	0.101	0.006	0.004
4	Special, low-carbon, aluminum-killed....	SiMn, FeMn	FeSi, Al	None	0.17	0.09	0.65	0.029	0.014	0.008	0.001
5	Low-carbon, silicon-killed.....	None	FeMn, FeSi	None	0.22	0.14	0.45	0.042	0.020	0.020	0.001
6	Medium-carbon, silicon-killed.....	Spiegel	FeMn, FeSi	None	0.43	0.20	0.47	0.027	0.014	0.012	<0.001
7	Open-hearth iron, rimming.....	None	Al	None	0.016	0.001	0.024	0.022	0.011	0.009	<0.001
8	Similar to No. 4 but higher in oxygen....	None	Al	Al	0.20	0.03	0.45	0.033	0.014	0.012	<0.001

with 1G emery paper and etched from 10 to 15 min. in 1:1 hydrochloric acid at 70° C. The characteristic pattern developed in each of the eight steels (Fig. 1) clearly indicated differences between the core and outer areas of most of the steels, but no significant difference could be detected in samples from different positions in the same rod. Two steels, Nos. 1 and 7, in which deep etching indicated definite segregation, were studied to see if the oxygen content was correspondingly nonuniform. Oxygen determinations were run by the vacuum-fusion method on samples representing: (1) a complete cross section of each rod and (2) the core, the outer areas having been removed in a lathe. The results were as follows: steel 1, the complete cross section (0.96-in. dia.), 0.019 per cent of oxygen; the core (0.357-in. dia.), 0.033 per cent of oxygen. Likewise, in iron 7 the complete cross section (1.25-in. dia.) contained 0.112 per cent of oxygen and the core (0.494-in. dia.) contained 0.128 per cent of oxygen. Evidently the segregation revealed by deep etching includes segregation of oxygen. The necessity for using a complete cross section of a rod for the sample in each determination of oxygen or oxides is evident.

An obvious precaution in the preparation of samples for the determination of oxygen or oxides is the removal of the oxygen-rich scale resulting from hot-rolling. To insure uniformity in this respect, it was recommended that each cooperator reduce the diameter of iron 7 to 1.25 in. and the diameter of each of the other steels to 0.95 in., in a lathe just before preparing the analytical samples.

At the completion of the exploratory examination the rods were cut into 1-ft. lengths, each being marked to identify its position in the original rod. Each 1-ft. length was cut into two 6-in. lengths, one for analytical samples and the other to be retained for reference. Bundles of eight 6-in. rods, one from each of the eight steels, were prepared for the cooperating laboratories.

Meanwhile correspondence had been conducted with laboratories in this country and abroad, that were known to be interested in the determination of oxygen in ferrous materials. By May 1, 1934, when the first bundles of samples were ready for distribution, 21 laboratories had agreed to participate. Additional laboratories subsequently expressed their desire to cooperate, so that the present summary (August, 1936) includes results from 34 laboratories, as follows: 20 in the United States, 5 in Great Britain, 4 in Germany, and one each in Canada, Italy, Japan, Russia and Sweden. The laboratories whose reports are the basis for the present summary are listed in Table 2, together with identification numbers and indications of the methods of analysis employed. Several of the laboratories reported results by more than one method of analysis. Consequently there are available 15 reports of determinations by the vacuum-fusion method, 11 by the iodine method, 7 by the electrolytic method, 4 by the hydrogen-reduction method, 3 by the chlorine method,

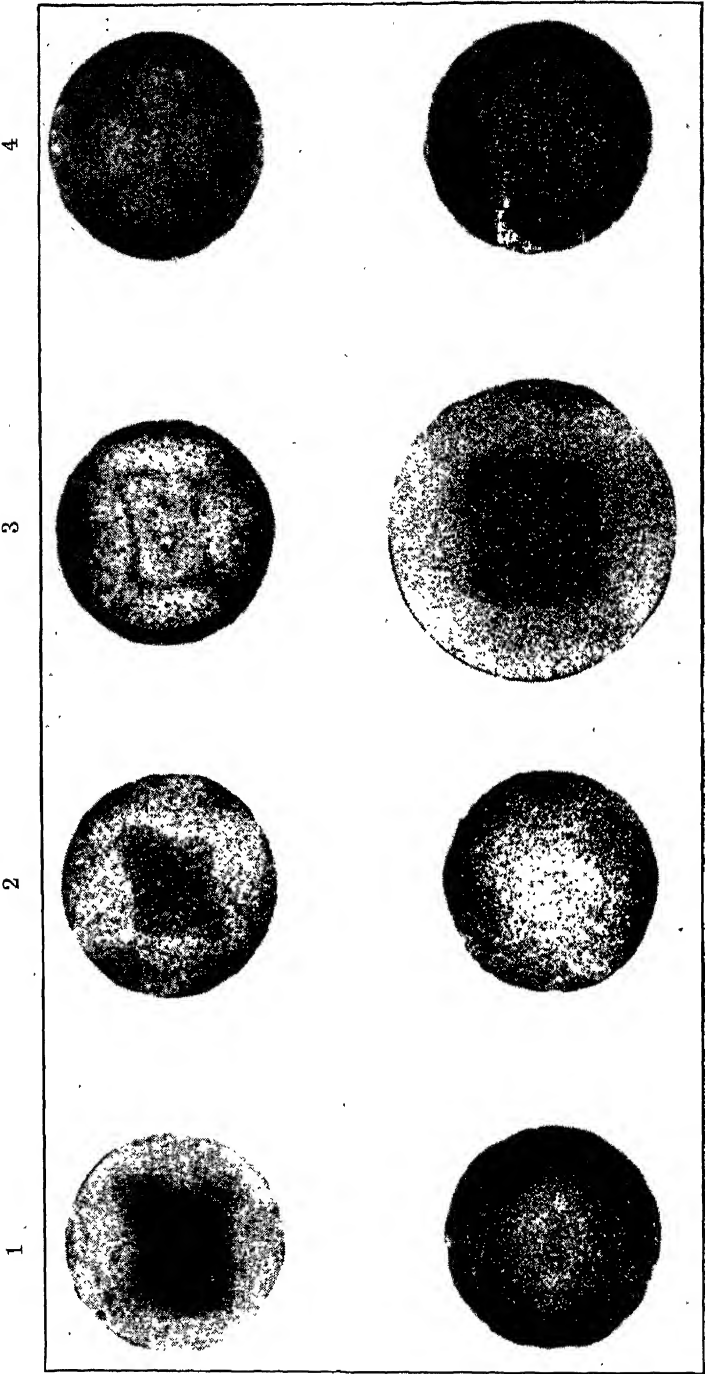


FIG. 1.—APPEARANCE OF THE EIGHT STANDARD SAMPLE STEELS AFTER DEEP ETCHING IN 1:1 HCl.  $\times 1$ .

TABLE 2.—Cooperating Laboratories and Methods Employed

Number of Cooperator	Laboratory	Method
1	Battelle Memorial Institute, Columbus, Ohio. S. Epstein, Metallurgist.	Microscopical examination and inclusion count. <i>Metals &amp; Alloys</i> (1931) 2, 186.
2	United States Steel Corporation, Kearny, N. J. John Johnston, Director of Research; T. E. Brower, B. M. Larsen.	Hydrogen-reduction method. <i>Trans. A.I.-M.E.</i> (1934) 113, 61.
3	Mining and Metallurgical Advisory Boards to the Carnegie Institute of Technology, Pittsburgh, Pa. C. H. Herty, Jr., Director of Research; J. F. Sanderson, B. E. Sockman.	Electrolytic method as described by Fitterer et al. U. S. Bur. Mines <i>Report of Investigations</i> 3205 (May, 1933).
4	Inland Steel Co., Indiana Harbor, Ind. Frank W. Scott.	Electrolytic method. <i>Ind. &amp; Eng. Chem., Anal. Ed.</i> (1932) 4, 121.
5	British (Guest Keen Baldwins) Iron and Steel Co. Ltd., Port Talbot, Wales. F. F. Hunting, Chief Metallurgist; N. Gray, Chief Chemist.	Hydrogen-reduction method. Sample melted with antimony and tin.
6	Babcock and Wilcox Tube Co., Beaver Falls, Pa. Newell Hamilton, Research Metallurgist.	Vacuum-fusion method. <i>Trans. A.I.M.E.</i> (1934) 113, 111.
7	Bethlehem Steel Co., Inc., Bethlehem, Pa. P. E. McKinney, Metallurgical Engineer; George F. Stammler.	Iodine method, essentially that of cooperator No. 13.
8	Department of Engineering Research, University of Michigan, Ann Arbor, Mich. John Chipman, Research Engineer; M. G. Fontana, C. L. Raynor.	Vacuum-fusion method. <i>Ind. &amp; Eng. Chem., Anal. Ed.</i> (1935) 7, 391.
9	English Steel Corporation, Ltd., Sheffield, England. T. R. Walker, Chief Research Chemist.	Iodine method of Cooperator No. 13. Nitric acid residue method. <i>Jnl. Iron and Steel Inst.</i> (1928) 113, 177.
10	Lukens Steel Co., Coatesville, Pa. W. G. Hampton, Metallurgical Engineer.	Iodine method. Solution by Willems' method. <i>Archiv. f. d. Eisenhüttenwesen</i> (1928) 1, 655; analysis of residue by method of cooperator No. 13.
11	Research Institute for Iron, Steel, and Other Metals, Sendai, Japan. T. Ishiware, Director; T. Yajima.	Vacuum-fusion method. Includes features of several procedures.
12	S K F Industries, Inc., Philadelphia, Pa. Haakon Styri, Director of Research.	Electrolytic method. <i>Trans. A.I.M.E.</i> (1933) 105, 185; <i>Metals &amp; Alloys</i> (1934) 5, 96.
13	Electro Metallurgical Co., Niagara Falls, N. Y. Thomas R. Cunningham.	Iodine method of Cunningham and Price. <i>Ind. &amp; Eng. Chem., Anal. Ed.</i> (1933) 5, 27.
14	Bell Telephone Laboratories, New York, N. Y. J. H. Seaff.	Vacuum-fusion method. <i>Metals &amp; Alloys</i> (1933) 4, 7.
15	Kaiser Wilhelm Institut für Eisenforschung, Düsseldorf, Germany. F. Körber, Director.	Vacuum-fusion method. <i>Mitt. Kaiser-Wilhelm Inst. f. Eisenforsch. Düsseldorf</i> (1931) 13, 215.
16	Ontario Research Foundation, Toronto, Canada. O. W. Ellis, Director of Metallurgical Research; J. R. Gordon, Research Metallurgist.	Chlorine method. <i>Ibid.</i> (1927) 9, 195. Iodine method of cooperator No. 13.
17	Kohle u. Eisenforschung GMBH Forschungs-Institut, Dortmund, Germany. E. H. Schulz, Director.	Chlorine method. <i>Mitt. Forsch. Inst. Ver Stahlwerke A. G. Dortmund</i> (1930) 1, 231; <i>Chem. Fabrik</i> (1929) 2, 51.
18	Metallografiska Institutet, Stockholm, Sweden. Carl Benedicks, Director; G. Phragmén, Metallographer.	Hydrogen-reduction method. <i>Stahl u. Eisen</i> (1920) 40, 812; <i>Archiv. f. d. Eisenhüttenwesen</i> (1929-30) 3, 459.
19	American Rolling Mill Co., Middletown, Ohio. A. H. Thomas, Supervisor, Service Testing Laboratories; D. L. Reck, Research Engineer; O. B. Ellis, Chemist.	Vacuum-fusion method. <i>Jernkontorets Ann.</i> (1931) 114, 549.
20	Fried. Krupp Aktiengesellschaft Gusstahlfabrik, Essen, Germany. P. Klinger, Chief Chemist.	Electrolytic method of cooperator No. 3. Iodine method of cooperator No. 13.
		Vacuum-fusion method, presumably. <i>Archiv. f. d. Eisenhüttenwesen</i> (1932) 6, 189. Analysis as described in <i>Stahl u. Eisen</i> (1925) 45, 1559.
		Chlorine method. <i>Archiv. f. d. Eisenhüttenwesen</i> (1933-34) 7, 618.
		Mercuric chloride method. <i>Ibid.</i> (1934-35) 8, 391.
		Electrolytic methods. (A), <i>Ind. &amp; Eng. Chem., Anal. Ed.</i> (1932) 4, 121; (B), <i>Jernkontorets Ann.</i> (1932) 116, 166.

TABLE 2.—(Continued)

Number of Cooperator	Laboratory	Method
21	Istituto Scientifico Tecnico Ernesto Breda, Milano, Italy.	Vacuum-fusion method. <i>Archiv f. d. Eisenhüttenwesen</i> (1932) 6, 189. Iodine method. Essentially method of cooperator No. 13.
22	United Steel Companies, Limited, Stocksbridge, England. T. Swinden, Director of Research.	Iodine method of Rooney and Stapleton. <i>Jnl. Iron and Steel Inst.</i> (1935) 131, 249
23	Westinghouse Electric and Manufacturing Co., East Pittsburgh, Pa. T. D. Yensen, Manager, Magnetic Division; Wilson Scott, N. A. Ziegler.	Vacuum-fusion method. <i>Trans. Amer. Electrochem. Soc.</i> (1932) 62, 109.
24	A. O. Smith Corporation, Milwaukee, Wis. S. L. Hoyt, Director of Metallurgical Research; M. A. Scheil, Research Metallurgist.	Fractional vacuum-fusion method. <i>Trans. A.I.M.E.</i> (1934) 113, 82. Microscopical examination. <i>Trans. A.I.M.E.</i> (1935) 116, 405.
25	Babcock and Wilcox Co., Barberton, Ohio. J. B. Romer, Chief Chemist.	Mercuric chloride method. <i>Archiv f. d. Eisenhüttenwesen</i> (1934-35) 8, 391.
26	School of Mines, Columbia University, New York, N. Y. William Campbell, Professor of Metallurgy; S. W. Poole.	Microscopical examination.
27	Department of Metallurgy, University of Sheffield, Sheffield, England. J. H. Andrew, Professor of Metallurgy.	Iodine and vacuum-fusion methods. <i>Iron and Steel Inst.</i> , 6th Report of the Heterogeneity of Steel Ingots (1935) Sec. 3, 50 and 61.
28	Youngstown Sheet and Tube Co., Youngstown, Ohio. G. A. Reinhardt, Director of Research and Metallurgy; Francis M. Walters, Jr., Research Engineer.	Vacuum-fusion method. <i>Nat. Bur. Stds Jnl. of Research</i> (1931) 7, 375.
29	National Bureau of Standards, Washington, D. C. H. S. Rawdon, Chief, Division of Metallurgy; J. G. Thompson, H. C. Vacher, H. A. Bright.	Vacuum-fusion method. <i>Nat. Bur. Stds Jnl. of Research</i> (1931) 7, 375. Iodine method of cooperator No. 13. Hydrochloric acid residue method. <i>Ibid</i> (1932) 9, 615.
30	War Department, Watertown Arsenal, Watertown, Mass. G. F. Jenks, Colonel, Ordnance Department, U. S. A., Commanding Officer; A. Sloan, P. R. Kesting, M. B. Gruzdis.	Iodine method of cooperator No. 13. Electrolytic method of cooperator No. 3.
31	National Physical Laboratory, Teddington, England. C. H. Desch, Superintendent, Metallurgy Department.	Iodine method of Rooney and Stapleton. <i>Jnl. Iron and Steel Inst.</i> (1935) 131, 249.
32	Central Institute of Metals, Leningrad, U. S. S. R. B. Selivanoff, General Scientific Manager; Gr. Weinberg, Metallurgist; M. Janowsky, Chief of the Chemical Laboratories.	Vacuum-fusion method. <i>Sloman. Iron and Steel Inst.</i> , 6th Report of the Heterogeneity of Steel Ingots (1935) Sec. 4, 71. Hydrogen-reduction method. Report of the Central Inst. of Metals (1935) 18, 449.
33	Illinois Steel Co., Chicago, Ill. M. A. Grossmann, Director of Research; Miss M. Baeyerzt.	Microscopical examination.
34	Institut für Eisenhüttenkunde der Technischen Hochschule, Aachen, Germany. W. Eilender, Director.	Vacuum-fusion method, graphite-spiral furnace.

2 by the mercuric chloride method, and one each by the nitric acid and hydrochloric acid residue methods. These reports represent more than 2000 analytical determinations. Three reports of microscopical examinations also are available.

#### REVIEW OF DATA OF COOPERATIVE TESTS

A brief summary of available data was distributed to the cooperators in December 1935, primarily to enable each cooperator to compare his results with those of others using the same method. The data likewise

were presented for discussion before the Iron and Steel Division in February 1936, and it was agreed that a critical review of these data could be better and more authoritatively accomplished by a small group, comprising experts in the various methods of analysis, rather than by one or two individuals. A subcommittee of the Iron and Steel Division was therefore appointed, as follows:

John Chipman, *Chairman* (American Rolling Mill Co.),  
J. J. Egan (Union Carbide and Carbon Research Laboratories),  
C. H. Herty, Jr. (Bethlehem Steel Company),  
S. L. Hoyt (A. O. Smith Corporation),  
John Johnston (United States Steel Corporation).

On May 14, 1936, the committee, with Messrs. Hoyt and Johnston represented by M. A. Scheil and B. M. Larsen, respectively, met with representatives of the National Bureau of Standards (J. G. Thompson, H. C. Vacher, H. A. Bright) and with the following who were present by invitation:

Thomas R. Cunningham (The Electro Metallurgical Company),  
Frank W. Scott (Inland Steel Co.),  
O. B. Ellis (American Rolling Mill Co.),

Louis Jordan (Assistant Secretary, American Institute of Mining and Metallurgical Engineers).

To facilitate the review of the data, the committee was divided into two sections to consider the data for the "hot" and "wet" methods of analysis, respectively, as follows:

*Hot Methods*, Messrs. Chipman, Larsen, Scheil, Jordan, Vacher, Thompson.

*Wet Methods*, Messrs. Herty, Egan, Cunningham, Scott, Ellis, Bright.

Since more data were available for the vacuum-fusion and iodine methods than for any of the others, attention was first directed to a review of these methods, data for other methods of analysis being reserved for subsequent consideration. After two days of intensive study of the two types of methods, the two sections combined for general discussion. The results of all the deliberations are summarized in the following paragraphs.

#### THE VACUUM-FUSION METHOD

The principles upon which the vacuum-fusion method, for the determination of total oxygen in iron or steel, is based, are briefly as follows:

The sample is melted in a graphite crucible contained in a highly evacuated furnace. Under these conditions, occluded and dissolved oxygen is liberated, and the various oxide and silicate combinations that exist in ferrous materials are rapidly and completely reduced. In the usual procedure, determination of the amount of carbon monoxide in the gases evolved from the sample furnishes a value for the total oxygen



content of the material but does not indicate the relative amounts of the various compounds of oxygen that were present. In the recently developed fractional vacuum-fusion method, values for the individual oxides are obtained by reduction of the sample in stages, at successively increased temperatures, with separate analysis of the gases evolved in each stage. The vacuum-fusion method permits the simultaneous determination of nitrogen and hydrogen, as well as oxygen, in a single sample.

TABLE 3.—*Percentages of Oxygen Obtained by the Vacuum-fusion Method*

Steel 1		Steel 2		Steel 3		Steel 4		Steel 5		Steel 6		Steel 7		Steel 8	
Per Cent	Co-operator	Per Cent	Co-operator	Per Cent	Co-operator	Per Cent	Co-operator	Per Cent	Co-operator	Per Cent	Co-operator	Per Cent	Co-operator	Per Cent	Co-operator
0.0215	6	0.018	15	0.0235	23	0.0055	6	0.014	23	0.0085	6	0.125	31	0.022	6
0.021	14	0.0175	27	0.023	27	0.005	24	0.013	6	0.008	29	0.112	15	0.022	27
0.021	28	0.016	29	0.021	24	0.004	15	0.012	24	0.0075	28	0.110	6	0.0195	23
0.020	20	0.016	18	0.020	31	0.004	27	0.011	29	0.007	15	0.110	8	0.019	15
0.020	31	0.016	31	0.0195	29	0.003	20	0.0105	27	0.006	24	0.107	29	0.019	31
0.0195	24	0.014	24	0.019	15	0.0025	28	0.010	15	0.006	27	0.107	14	0.0185	28
0.019	34	0.014	34	0.017	8	0.0025	18	0.010	31	0.0055	8	0.107	34	0.018	14
0.019	29	0.013	8	0.017	14	0.0025	14	0.0085	8	0.0055	18	0.105	28	0.017	29
0.018	15	0.013	20	0.0145	28	0.002	29	0.008	18	0.005	21	0.105	18	0.017	18
0.018	23	0.013	28	0.014	21	0.002	31	0.0075	21	0.005	34	0.103	24	0.016	8
0.0175	11	0.0125	11	0.014	18	0.0015	8	0.007	14	0.005	31	0.103	23	0.0155	24
0.017	8	0.012	21	0.014	20	0.001	21	0.007	20	0.005	20	0.100	21	0.015	20
0.016	18	0.0115	6	0.013	11	0.001	11	0.0065	11	0.004	14	0.100	20	0.0145	34
0.0145	21	0.0115	23	0.0115	6	0.0000	23	0.0065	28	0.003	11	0.100	27	0.0145	21
0.009	27	0.004	14	0.011	34			0.0065	34	0.003	23	0.096	11	0.014	11

Fifteen reports of determinations by the vacuum-fusion method were available for consideration. Some of the cooperators reported the results of individual determinations, others reported only one value for each steel. The data are summarized in Table 3, the values given being either the preferred values of each cooperator or averages of all the determinations when a preferred value was not indicated. These data differ in some respects from the tabulated data in the preliminary report to the cooperators. Two additional sets of results have been included; some errors in the originally reported values have been corrected or revisions have been made to include results of additional determinations; some of the averaged values have been rounded to eliminate meaningless fractions of one thousandth of one per cent.

The review of the vacuum-fusion data proceeded along three lines:

1. Arbitrary establishment of a range of "acceptable" results for each steel, by eliminating scattered high and low results.
2. Statistical study to determine the apparatus and procedures most consistently yielding results within the acceptable ranges.

3. Detailed study of apparatus and procedure of each cooperator for possible explanation of the ability or failure to obtain consistently acceptable results.

Many of the final conclusions have been based upon consideration of all the foregoing criteria, but for convenience in this report the three items will be discussed separately.

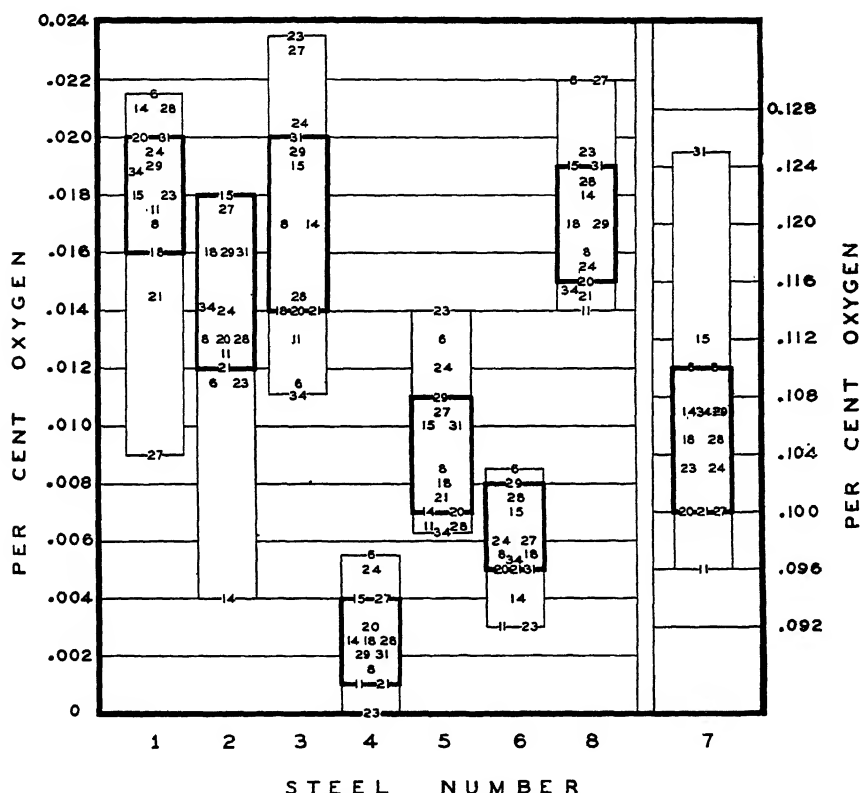


FIG. 2.—VACUUM-FUSION METHOD, DETERMINATIONS OF TOTAL OXYGEN.

Numbers are those of the cooperators and acceptable values are those within the heavily lined boxes.

The first consideration was that the range of the reported results for each steel was too great to be acceptable. Since it is evident that no cooperator obtained results consistently higher, or lower, than the others for all eight steels and that, in general, the relative position of each cooperator within the groups in Table 3 varies considerably from steel to steel, the large ranges can be considered to be the result of individual experimental errors rather than of consistent differences in apparatus or procedure. It is therefore legitimate to eliminate arbitrarily the scattered results, either high or low, in order to obtain for each steel a narrowed range including the results of a majority of the cooperators.

Fig. 2 illustrates the elimination process employed to establish an acceptable range of values for each steel. The numbers refer to the cooperators; the value obtained by each being indicated by the position with reference to the ordinate scale. Acceptable values are those within the heavily lined box in each grouping. Possible explanation for the elimination of many discarded values will be developed in the consideration of individual apparatus and procedure.

TABLE 4.—*Acceptable Ranges and "Best" Values of Oxygen Content According to the Vacuum-fusion Method of Analysis*

Steel No.	Acceptable Range, Per Cent	"Best" Value, Per Cent
1	0.016 to 0.020	0.018
2	0.012 to 0.018	0.017
3	0.014 to 0.020	0.017
4	0.001 to 0.004	0.002
5	0.007 to 0.011	0.009
6	0.005 to 0.008	0.007
7	0.100 to 0.110	0.106
8	0.015 to 0.019	0.017

For all the steels except No. 2 the scattered high and low values were discarded. For steel 2, which has a manganese content of more than 1 per cent, it was considered doubtful that any cooperator would obtain too high a result. Consequently, only the low results were eliminated. The acceptable ranges thus defined for the steels are shown in Table 4. Such ranges would be considered satisfactory in determinations of corresponding amounts of elements such as carbon, sulphur and manganese, for which the analytical methods are much more standardized than those for the determination of oxygen. Table 4 also shows the values selected by the reviewing committee as the "best" value for the oxygen content of each steel according to the vacuum-fusion method of analysis.

As is evident from Fig. 2, the acceptable range includes a majority of the reported values for each steel, but the personnel of the acceptable majority varies from steel to steel. Plausible explanations for many of these deviations from acceptable results can be derived from consideration of the details of apparatus and procedure of the individual cooperators. Some of these details, compiled from the reports of the cooperators and the published references cited in Table 2, are shown in Table 5.

From the fact that four cooperators, Nos. 8, 18, 20 and 29, obtained results lying within the acceptable range for each of the eight steels, it is evident that acceptable results can be obtained in spite of considerable variation in apparatus and procedure. Cooperator 20 used a graphite-spiral furnace; the other three used high-frequency induction furnaces.

TABLE 5.—Details of Vacuum-fusion Procedures

Cooperator	Furnace	Operating Temperature, Deg. C.	Crucible Support	Thermal Insulator	Blank Correction		Sample Weight, Grams	Number of Samples in Crucible	Surface of Melt	Average Temperature of Run, Min.	Gas Analysis	Remarks
					CO per Hr., a.c.	Per Cent, Oxygen <sup>c</sup>						
6	High-frequency induction	1650	Pedestal	Sillimanite	<0.08	<0.00015	15	6	Open		Low pressure gravimetric	
8	High-frequency induction	1650	Graphite-MgO	Graphite	<0.2	<0.0002	15 <sup>d</sup>	1-2	Graphite float	15	Low pressure, volumetric	
11	High-frequency induction	1650	Quartz	Molybdenum	0.066-0.08	<0.0002	8	5	Funnel top	15	Atmospheric pressure	
14	High-frequency induction	1600 <sup>a</sup>	BeO	Aluminum	0.2-3.1	0.0003-0.003	14-27		Graphite sleeve		Selective freeing	
15	High-frequency induction	1600	Pedestal	None				1	Open		Atmospheric pressure	100 grams Fe in crucible.
18	High-frequency induction	1650	Pedestal	Water-cooled tube	0.06	<0.0002	35 <sup>a</sup>		Graphite filter and valve	25	Atmospheric pressure (Oberhofer)	
20	Graphite-spiral.....	1900			0.6	0.001	20	3		30	Atmospheric pressure (Oberhofer)	Low-Mn Fe in crucible.
21	Graphite-spiral.....	1750			0.16-0.2	<0.001	7			30	Atmospheric pressure (Meyer and Castro)	
23	High-frequency induction	1700 <sup>a</sup>	Pedestal	None	3.3	0.003	10	Several	Open	20	Selective freeing	Melts sample with tin.
24	High-frequency induction	1570	Zirconia	Sillimanite	0.77	0.0033	11 <sup>d</sup>	1		150 <sup>a</sup>	Atmospheric pressure	Nine radiation screens.
27	Graphite-spiral.....	1700			0.08-0.2	<0.0003	15 <sup>d</sup>	Several	Open	20	Atmospheric pressure	
28	High-frequency induction	1650	Graphite-BeO	Graphite				5	Graphite guide tube	15	Low pressure, volumetric	
29	High-frequency induction	1650	Graphite-BeO	Graphite	0.3-0.8	<0.001	15	1-5	Graphite guide tube	15	Low pressure, volumetric	
31	High-frequency induction	1550	Pedestal <sup>b</sup>	Graphite powder and water-cooled tube	0.014-0.05	<0.0001	15 <sup>f</sup>	Several	Graphite valve	20	Atmospheric pressure	
34	Graphite-spiral.....											Other details not yet available.

<sup>a</sup> Cooperators 14, 23 and 24 introduce the sample into a cooled crucible and subsequently raise the temperature to the indicated operating temperature. Other cooperators introduce samples at the indicated temperatures.

<sup>b</sup> Cooperator 31 surrounds the pedestal and the crucible with powdered graphite.

<sup>c</sup> Based on weight of sample used and time of a determination.

<sup>d</sup> Semi-disk.

<sup>e</sup> 1-in. rods were forged to about 1 cm. diameter to provide sample material.

<sup>f</sup> Samples not representative of complete cross sections of the 1-in. rods.

<sup>g</sup> Total time for determination of FeO, MnO, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> fractions.

Operating temperatures ranged from 1550° C. for No. 18 to 1900° C. for No. 20. The type of crucible support, thermal insulation of the crucible, weight of sample, and the method employed for analysis of the evolved gases, varied considerably in these four procedures. Three of the four employed large furnace connections and four-stage, high-capacity diffusion pumps for rapid evacuation of the evolved gases from the furnace chamber, whereas cooperator 8 obtained acceptable results with a two-stage pump and somewhat constricted furnace connections. Protection of the quartz furnace tube by an external water jacket, instead of internal radiation screens, yielded acceptable results for cooperator 18, although it is interesting to note that Thanheiser and Brauns<sup>2</sup> recently reported that the interference of manganese, leading to low recoveries of oxygen, was more severe when the furnace tube was water-jacketed than when it was less drastically cooled by means of a coil of copper tubing.

The four procedures that yielded acceptable results for all eight steels have the following characteristics in common: (1) a low blank correction for the apparatus, (2) precautions against interference by manganese, and (3) precautions against spattering of the molten sample. The importance of these three characteristics, common to all four of these procedures, deserves emphasis. A low blank correction, equivalent to not more than 0.001 per cent of oxygen per determination, is a prerequisite of satisfactory operation; larger or variable blank corrections are unsatisfactory for the determination of small amounts of oxygen.

It is the opinion of the reviewing committee that the presence of manganese in the sample causes some degree of interference in many of the procedures employed in this cooperative analysis because of absorption of gas by manganese vapor or sublimate. Higher recoveries of oxygen are obtained when the following conditions obtain: (1) the sample is rapidly melted, (2) the gases evolved from the sample are rapidly removed from the highly evacuated furnace chamber, and (3) the manganese content of metal in the crucible is kept low either by dilution of the sample with manganese-free iron or by the use of a fresh crucible for each sample. Conversely, low recoveries of oxygen from samples that contain manganese are obtained if the sample is melted slowly, if the evolved gases are not removed rapidly enough, or if several manganese-rich samples are run consecutively in the same crucible. Cooperator 20 remarked that "the oxygen values for the two manganese-rich samples, 2 and 3, are perhaps somewhat low in spite of our precautions." On account of the tendency towards manganese interference, the "best" value for the oxygen content of steel 2 (1.15 per cent of manganese) is probably at or near the top of the acceptable range; for each of the other seven steels, the "best" value is approximately the mean of the acceptable values.

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<sup>2</sup> *Archiv f.d. Eisenhüttenwesen*, (1935-36) 9, 435.

Spattering as a result of gas evolution from the sample during melting or shortly thereafter may result in either high or low errors of considerable magnitude. If the spattered globules of molten metal come in contact with refractory oxides of the radiation screen or quartz furnace tube, a reaction resulting in the formation of CO may occur and cause a high value for oxygen. On the other hand, if the portion thrown out from the crucible falls to the cold bottom of the furnace tube, the oxygen of that portion of the sample is lost. The apparatus of each of the four cooperators, who obtained consistently satisfactory results, was arranged to prevent loss of molten spatters or their contact with hot refractory oxides. No. 8 used a graphite float and No. 18 a graphite filter to prevent the spattered material from leaving the crucible; No. 20 apparently used a deep crucible covered with a graphite funnel in a graphite-spiral furnace which did not contain any refractory oxides. In the apparatus of cooperator 29, a thin-walled graphite tube extended from the top of the crucible to the bottom of the guide tube through which the samples were dropped. With this arrangement, any spattered particles struck the inner surface of the graphite tube and dropped back into the crucible. Only rarely would a spattered particle be evolved with sufficient velocity to reach the guide tube.

Spattering is probably one of the principal causes for the erratic results of individual determinations and for the divergence between the results of different cooperators. It is significant that the greatest divergence of reported results is for open-hearth iron 7, which has the largest oxygen content and consequently the greatest tendency to spatter. The results for steel 3, although less divergent than the results for iron 7, are more divergent than those of other steels of similar oxygen content. However, steel 3 is relatively high in nitrogen, hence the total volume of gases evolved is appreciably greater than that from other steels of similar oxygen content. Consequently the divergence of results for steel 3 also may be ascribed in part to spattering. It has been previously mentioned that gradual melting of the sample is sometimes employed to reduce the tendency to spatter, but this procedure apparently increases the susceptibility to manganese interference.

Considering next the two cooperators, Nos. 15 and 31, whose results fall within the acceptable ranges for all but one of the steels, we find that for iron 7 the results of cooperator 15 are slightly high, whereas those of cooperator 31 are decidedly high. The results of cooperator 15 fall consistently in the upper portions of the acceptable ranges of the other steels; there is no obvious explanation for the slightly high results for iron 7, unless it is the result of spattering onto the furnace tube. On the other hand, the high results of cooperator 31 for iron 7 are undoubtedly the result of improper sampling. Each sample used by this cooperator was a small cylinder whose long axis was a transverse diameter of the original

rod. Such a sample does not represent a complete cross section of the original rod but instead contains an undue proportion of core material which, in iron 7, is relatively high in oxygen. In the exploratory analyses (p. 249) it was found that the oxygen content of a sample representing a complete cross section of iron 7 was 0.112 per cent, whereas a sample corresponding roughly with the segregated core area contained 0.128 per cent. The latter value is in excellent agreement with that obtained from the transverse cylindrical samples of cooperator 31. It might be predicted, on the basis of the results of the exploratory analyses, that the use of these nonrepresentative samples would lead to high results for steel 1 as well as for iron 7. However, this was not so; the results of cooperator 31 are within the acceptable range, although frequently at or near the top, for all the steels except No. 7. In describing his procedure, this cooperator stated that manganese contents up to 12 per cent and aluminum up to at least 2.5 per cent do not interfere with the results of the first determination, and that when manganese is present in appreciable amounts the furnace is cleaned after each determination. The diffusion pump is always kept evacuated and it was stated that opening the pump to the atmosphere resulted in absorption of gas on the walls of the pump and this absorbed gas could be completely removed only after several days of evacuation.

The remaining cooperators are considered in numerical order. It is evident that the results of cooperator 6 are generally high, except for steels 2 and 3. Spattering of the melt onto the sillimanite radiation screen may account for some of the high results; manganese interference may be blamed for the low results for steels 2 and 3.

The results of cooperator 11 are generally low in comparison with the majority, perhaps because of loss by spattering. Ericson and Benedicks<sup>3</sup> reported that spattering occurred in crucibles similar to those used by cooperator 11. Since in the apparatus the crucible was supported on and centered by small blocks of quartz, contact of quartz with the hot graphite crucible might be expected to result in the evolution of carbon monoxide. That this did not occur to any appreciable extent is indicated by the low blank correction for the apparatus and by the fact that low recoveries of oxygen from the samples were generally obtained.

The results of cooperator 14 are within the acceptable ranges for five of the steels, with only steel 2 more than 0.001 per cent away from the acceptable values. The reported blank corrections varied from steel to steel. The low result for steel 2 presumably represents the interference of manganese, intensified by introducing the sample into a cooled crucible with subsequent slow melting. Cooperator 14 suggested that the slow melting procedure may promote the agglomeration of silica or silicates, if present, into large particles, which are reduced slowly and with

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<sup>3</sup> *Jernkontorets Ann.* (1931) 114, 567.

difficulty. Low recoveries of oxygen, therefore, might be obtained from slowly melted samples that contained silica or silicates, irrespective of the manganese content.

Cooperator 21 used a graphite-spiral furnace and expressed dissatisfaction with the results obtained. Changing the apparatus by increasing the diameter and decreasing the length of the connections between furnace and train slightly improved the operation. Errors were ascribed by this cooperator to: (1) spattering of the molten bath and (2) absorption of gas by metallic vapors and sublimates, by graphite ash, and by the graphite itself in the cooler portions of the furnace.

The apparatus of cooperator 23 appears to be subject to criticism for the following reasons: (1) a high blank correction, (2) slow melting of the sample, (3) use of a single crucible for several samples, and (4) spattering from the open crucible, which may have attacked the silica furnace tube or dropped to the bottom of the tube and been lost. Combinations of these factors can account for the lack of agreement in some of the duplicate determinations and for the considerable variation in the relative position of the results with respect to those of other cooperators for the different steels.

The fractional vacuum-fusion method is represented in this report by the results of only one cooperator, No. 24. While the values obtained for total oxygen from the separate fractions are usually within the acceptable range, they are slightly high for steels 3, 4 and 5. Comparison of the values obtained for the separate fractions with the results of the wet methods is given in a later section.

The results of cooperator 27 are within the acceptable ranges except that those for steel 1 are low and those for steels 3 and 8 are high. Spattering from the open crucible may be the cause of the low results for steel 1. An unusual feature of the apparatus used is the set of nine radiation screens to retain the heat developed in the graphite spiral. The mass of hot graphite appears to be a potential source of error. Cooperator 27 stated his belief that with this apparatus, with its large-diameter furnace outlet and rapid removal of the gases by means of a high-capacity pump, interference from manganese contents up to 3 per cent or from aluminum contents up to 2 per cent is avoided. The high values obtained for steels 2 and 3 tend to substantiate this belief.

Equipment for vacuum-fusion analyses was installed only recently by cooperator 28. Average results within the acceptable range were obtained for six of the eight steels, although the divergence between duplicate determinations undoubtedly will be decreased with additional experience in the operation of the apparatus.

The receipt of the report of cooperator 34 was belated; details of the apparatus and procedure are not at present available, except that a graphite-spiral furnace was used.



*Recommendations for Determination of Oxygen by Vacuum-fusion Method*

A study of the results and of the apparatus and procedures, according to the information available in these cooperative analyses, leads to the following recommendations for the determination of oxygen by the vacuum-fusion method:

1. *Furnace Construction*.—Either high-frequency induction furnaces or a graphite-spiral resistor may be used. The presence of refractory oxides in the furnace chamber is undesirable, particularly if they are hot or in contact with hot graphite; beryllium oxide appears to be least objectionable.

2. *Analysis of Evolved Gases*.—The selection of a procedure and apparatus for the analysis of the gases evolved from the sample is apparently a matter of personal preference. The determination may be made volumetrically or gravimetrically, at low pressure or at atmospheric pressure, or by selective freezing.

3. *Procedure*.—Complete reduction of the oxides in these steels can be obtained in a reasonable time at temperatures as low as 1550° C. Preliminary "outgassing" of the furnace is accomplished at a temperature about 200° C. higher than the operating temperature. The pressure in the furnace at operating temperature should be 0.001 mm. Hg, or less, at the beginning of a determination. The blank correction for the apparatus should not exceed 0.001 per cent of oxygen per determination. The size of the sample depends upon the storage capacity of the apparatus and on the oxygen content of the material, but the sample must be representative. Spattering of the melting sample or of the molten bath should be prevented, but a satisfactorily reliable and convenient means of accomplishing this end has not yet been developed. The evolved gases should be removed rapidly and completely from the furnace chamber to avoid secondary reactions with the walls and contents of the furnace. A four-stage, mercury-diffusion pump of high capacity is frequently employed; constricted or relatively long connections between the furnace and the diffusion pump are not recommended.

4. *Manganese Interference*.—The presence of 0.5 per cent or more manganese constitutes a potential source of error in the apparatus generally used, either as a result of the presence of manganese as vapor in the furnace chamber or condensed on the furnace walls, or both. Established precautions to minimize the error from this source include: (a) the rapid and complete removal of evolved gases from the furnace chamber, (b) the use of a fresh crucible for each determination or dilution of the sample with manganese-free iron, (c) frequent cleaning of the furnace chamber. The minimum manganese content that will produce a noticeable error apparently varies with the construction of the apparatus and with the procedure. Two of the cooperators, Nos. 27 and 31, believe that their

procedures are free from error by interference from manganese content up to 3 and 12 per cent, respectively. Experiments on steel 2 at the National Bureau of Standards (unpublished) showed that two and sometimes three consecutive samples could be melted in the same crucible without appreciable error from manganese interference, provided that a high-capacity pump was used. On the other hand, when a pump of lower capacity was used, with somewhat higher furnace pressure, error from this source was noticeable in the second determination. It was also found that the determination of oxygen in steel 2 was affected somewhat by the

TABLE 6.—*Determinations of Nitrogen*

Nitrogen, Per Cent								
Steel No.....	1	2	3	4	5	6	7	8
Vacuum-fusion method:								
Cooperator 8.....	0.0025	0.0044	0.015	0.005	0.004	0.005	0.0045	0.004
11.....	0.0024	0.0024	0.014	0.0046	0.004	0.004	0.003	0.003
14.....	0.0019	0.0038	0.011	0.0035	0.003	0.0035	0.0055	0.0035
18.....	0.003	0.005	0.010	0.0088	0.006	0.005	0.008	0.005
24.....	0.003	0.003	0.015	0.002	0.002	0.003	0.004	0.0025
29.....	0.003	0.005	0.016	0.006	0.005	0.006	0.005	0.005
Solution-distillation method:								
Cooperator 2.....	0.003	0.006	0.016	0.005	0.004	0.005	0.005	0.004

TABLE 7.—*Determinations of Hydrogen*

Hydrogen, Per Cent								
Steel No.....	1	2	3	4	5	6	7	8
Cooperator 11..	0.00014	0.00016	0.00013	0.00007	0.00009	0.00007	0.00054	0.00017
18..	0.0001	0.0001	0.0001	0.0001	0.00005	0.00004	0.0003	0.0003
24..	0.0006	0.0008	0.0006	0.0003	0.0005	0.0003	0.0001	0.0003
29..	0.00002	0.00009	0.0002	0.0002	0.0002	0.0003	0.0004	0.00015

size of the sample, slightly higher values being obtained from the smaller samples. A possible explanation is that they melted more rapidly and the gas evolution was completed before appreciable evolution of manganese vapor occurred. This appears to be additional evidence of the usefulness of rapid melting of the sample for minimizing error from interference by manganese.

#### *Determinations of Nitrogen and Hydrogen*

Several cooperators reported results for nitrogen and hydrogen as well as for oxygen. These are summarized in Tables 6 and 7. The results

of different cooperators for nitrogen are in satisfactory agreement, allowance being made for an occasional high or low result. Low values may be the result of loss of the sample by spattering; high results may indicate nitride segregation. The good agreement of the single set of results by the solution-distillation method with those obtained by vacuum fusion indicate that both methods are dependable in determining the nitrogen content of these steels.

The results of the four cooperators who determined hydrogen by the vacuum-fusion method indicate that the hydrogen content for each of the eight steels is less than 0.001 per cent.

### THE IODINE METHOD

In the iodine method for determining oxides in steel, the sample is treated with a suitable solution of iodine. Iron, silicon and manganese are dissolved and a residue of carbonaceous material (carbides in certain cases) and unattacked oxides remains.

In the procedure described by Cunningham and Price (see reference, Table 2, cooperator 13), a sample weighing from 5 to 10 grams is treated at 3° to 5° C. in a stoppered flask with an aqueous solution of iodine in ferrous iodide<sup>4</sup>. By the method of Rooney and Stapleton (see reference, Table 2, cooperator 31) the sample is treated with a solution of iodine in anhydrous methyl alcohol (70 grams of iodine in 600 ml. of alcohol). Rather elaborate precautions are necessary to exclude all moisture and oxygen from the solvent and containers while the steel is dissolving and during filtration of the resulting solution. Willems (see reference, Table 2, cooperator 10) has recommended the use of a solution of iodine in absolute ethyl alcohol and filtration through an ultrafilter.

The proponents of the alcoholic iodine solutions claim that higher recoveries of oxides of iron and manganese are obtained with these solvents than with aqueous solutions of iodine in ferrous and potassium iodide.

The values for  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{MnO}$  and  $\text{FeO}$  obtained by the cooperators are given in Tables 8, 9, 10 and 11<sup>5</sup>. Reports were submitted by 12 cooperators, though not all reported values for all of the eight steels. Eight cooperators used an aqueous iodine solvent, essentially the procedure described by Cunningham and Price; three used a solution of iodine in

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<sup>4</sup> Prepared as follows: To 5 grams of plain carbon-steel drillings in a 300-ml. Erlenmeyer flask are added 25 ml. of water, 4 grams of ammonium citrate and 30 grams of iodine. The flask is shaken for several minutes in ice water and then 30 grams of additional iodine is added. The shaking is continued until all the iodine has dissolved, whereupon the solution is filtered. The total volume of the filtrate and washings should not exceed 75 ml., and this amount of solution is sufficient for a 5-gram sample. In larger samples, proportionately more solvent is used.

<sup>5</sup> Total Al, Si, Mn and Fe in the insoluble residues are reported as the single oxides, which may exist in the steel as such, or in combination as silicates or spinels.

TABLE 8.—*Determinations of  $Al_2O_3$  by the Iodine Method*

Steel 1			Steel 2		Steel 3		Steel 4		Steel 5		Steel 6		Steel 7		Steel 8	
Per Cent	Coop- erator		Per Cent	Coop- erator	Per Cent	Coop- erator	Per Cent	Coop- erator	Per Cent	Coop- erator	Per Cent	Coop- erator	Per Cent	Coop- erator	Per Cent	Coop- erator
CUNNINGHAM AND PRICE PROCEDURE																
0.010	9	0.039	9	0.021	9	0.025	9	0.016	9	0.038	9	0.020	9	0.032	29	
0.005	30	0.004	30	0.006	16	0.011	21	0.002	21	0.005	7	0.018	21	0.028	9	
0.003	21	0.003	21	0.005	21	0.007	7	0.002	29	0.003	21	0.014	16	0.027	7	
0.002	19	0.002	29	0.003	30	0.0056	29	0.000	7	0.002	30	0.004	19	0.025	30	
0.0003	29	0.001	19	0.002	19	0.004	16	0.000 <sup>a</sup>	16	0.000 <sup>a</sup>	16	0.0013	29	0.017	21	
0.000	7	0.000	7	0.000	7	0.003	30	0.000	30			0.000	7	0.016	16	
0.000 <sup>a</sup>	16	0.000 <sup>a</sup>	16	0.000	29	0.0024	19					0.000	30	0.012	19	
ROONEY AND STAPLETON PROCEDURE																
0.0037	22	0.016	31	0.021	27	0.008	27	0.0034	22	0.0042	22	0.022	27	0.033	22	
0.002	27	0.0065	22	0.0075	22	0.0066	31	0.0023	31	0.0026	31	0.012	22	0.031	27	
		0.003	27	0.000 <sup>b</sup>	31	0.0049	22	0.001	27	0.001	27	0.000	31			
WILLEMS' METHOD																
0.000 <sup>a</sup>	10	0.000 <sup>a</sup>	10	0.010	10	0.000 <sup>a</sup>	10	0.003	10	0.000 <sup>a</sup>	10	0.005	10	0.020	10	
SELECTED VALUE																
0.002, $\pm 0.002$		0.002, $\pm 0.002$		0.002, $\pm 0.002$		0.006, $\pm 0.002$		0.002, $\pm 0.002$		0.002, $\pm 0.002$		0.002, $\pm 0.002$		0.030, $\pm 0.003$		

<sup>a</sup> Reported by dash. It is assumed that a determination was made and no detectable amount found.<sup>b</sup> Reported as trace.

TABLE 9.—*Determinations of SiO<sub>2</sub> by the Iodine Method*

Steel 1		Steel 2		Steel 3		Steel 4		Steel 5		Steel 6		Steel 7		Steel 8	
Per Cent	Coop- erator	Per Cent	Coop- erator	Per Cent	Coop- erator	Per Cent	Coop- erator	Per Cent	Coop- erator	Per Cent	Coop- erator	Per Cent	Coop- erator	Per Cent	Coop- erator
CUNNINGHAM AND PRICE PROCEDURE															
0.018	9	0.041	9	0.037	9	0.015	9	0.049	9	0.049	9	0.012	9	0.040	9
0.005	30	0.012	21	0.012	30	0.015	30	0.020	30	0.014	30	0.011	30	0.010	30
0.005	16	0.012	30	0.007	19	0.008	16	0.019	16	0.010	13	0.004	21	0.005	16
0.005	21	0.010	16	0.006	7	0.004	21	0.015	13	0.009	16	0.002	16	0.0025	7
0.0022	29	0.006	29	0.005	13	0.002	7	0.015	29	0.008	21	0.002	19	0.002	21
0.0015	13	0.006	7	0.005	29	0.0018	13	0.013	7	0.006	7	0.0013	29	0.002	19
0.000	7	0.006	13	0.004	21	0.0012	29	0.012	21			0.000	7	0.0007	29
				0.003	16	0.0005	19					0.000 <sup>a</sup>	13	0.000 <sup>a</sup>	13
ROONEY AND STAPLETON PROCEDURE															
0.0034	22	0.027	22	0.014	22	0.0037	27	0.021	27	0.011	22	0.0013	22	0.0055	27
0.0027	27	0.021	31	0.013	31	0.0016	22	0.017	22	0.011	31	0.0009	27	0.0026	22
		0.0091	27	0.0015	27	0.0013	31	0.016	31	0.009	27	0.000 <sup>a</sup>	31		
WILLEMS' METHOD															
0.000 <sup>a</sup>	10	0.012	10	0.012	10	0.015	10	0.007	10	0.000 <sup>a</sup>	10	0.000 <sup>a</sup>	10	0.006	10
SELECTED VALUE															
0.003, ±0.002	0.009, ±0.003	0.005, ±0.002	0.002, ±0.002	0.016, ±0.003	0.009, ±0.003	0.002, ±0.002	0.009, ±0.003	0.002, ±0.002	0.003, ±0.002	0.002, ±0.002	0.003, ±0.002	0.002, ±0.002	0.003, ±0.002	0.003, ±0.002	0.003, ±0.002

<sup>a</sup> Reported by dash.

TABLE 10.—*Determinations of MnO by the Iodine Method*

Steel 1			Steel 2			Steel 3			Steel 4			Steel 5			Steel 6			Steel 7			Steel 8		
Per Cent	Coop- erator		Per Cent	Coop- erator		Per Cent	Coop- erator		Per Cent	Coop- erator		Per Cent	Coop- erator		Per Cent	Coop- erator		Per Cent	Coop- erator		Per Cent	Coop- erator	
CUNNINGHAM AND PRICE PROCEDURE																							
0.013	30	0.029	9	0.025	9	0.007	30	0.010	9	0.015	9	0.015	9	0.030	13	0.006	30	0.030	13	0.006	30	0.030	13
0.003	21	0.007	30	0.021	16	0.0065	9	0.009	30	0.011	16	0.011	16	0.030	7	0.0048	9	0.030	7	0.0048	9	0.030	7
0.0025	9	0.005	16	0.013	21	0.006	16	0.007	16	0.011	30	0.011	30	0.027	19	0.0035	16	0.027	19	0.0035	16	0.027	19
0.002	7	0.005	21	0.012	30	0.002	13	0.006	21	0.007	21	0.007	21	0.026	9	0.002	7	0.026	9	0.002	7	0.026	9
0.002	16	0.0023	13	0.0093	13	0.0003	29	0.003	7	0.005	13	0.005	13	0.022	21	0.002	21	0.022	21	0.002	21	0.022	21
0.002	29	0.0023	29	0.008	29	0.000	7	0.0022	13	0.004	7	0.0022	13	0.021	29	0.0015	29	0.021	29	0.0015	29	0.021	29
0.0014	13	0.002	7	0.0055	7	0.000	21	0.002	29			0.002	29	0.021	30	0.0012	13	0.021	30	0.0012	13	0.021	30
ROONEY AND STAPLETON PROCEDURE																							
0.044	22	0.041	27	0.172	31	0.0061	31	0.011	31	0.012	31	0.012	31	0.027	31	0.025	27	0.027	31	0.025	27	0.027	31
0.000 <sup>a</sup>	27	0.039	31	0.141	22	0.0057	22	0.0087	22	0.011	22	0.0087	22	0.023	22	0.0074	22	0.023	22	0.0074	22	0.023	22
		0.036	22	0.016	27	0.000 <sup>a</sup>	27	0.005	27	0.002	27	0.005	27	0.019	27			0.019	27				
WILLEMS' METHOD																							
0.008	10	0.0056	10	0.205	10	0.000 <sup>a</sup>	10	0.005	10	0.029	10	0.005	10	0.069	10	0.0026	10	0.029	10	0.0026	10	0.029	10
SELECTED VALUE																							
0.002, ±0.002	0.004, ±0.002	0.012, ±0.004	0.002, ±0.002	0.004, ±0.002	0.008, ±0.003	0.025, ±0.005	0.003, ±0.002	0.002, ±0.002	0.004, ±0.002	0.008, ±0.003	0.025, ±0.005	0.003, ±0.002	0.002, ±0.002	0.004, ±0.002	0.008, ±0.003	0.025, ±0.005	0.003, ±0.002	0.002, ±0.002	0.004, ±0.002	0.008, ±0.003	0.025, ±0.005	0.003, ±0.002	0.002, ±0.002

<sup>a</sup> Reported by dash.

TABLE 11.—*Determinations of FeO by the Iodine Method*

Steel 1		Steel 2		Steel 3		Steel 4		Steel 5		Steel 6		Steel 7		Steel 8	
Per Cent	Coop-erator	Per Cent	Coop-erator	Per Cent	Coop-erator	Per Cent	Coop-erator	Per Cent	Coop-erator	Per Cent	Coop-erator	Per Cent	Coop-erator	Per Cent	Coop-erator
CUNNINGHAM AND PRICE PROCEDURE															
0.015	30	0.024	16	0.015	13	0.018	30	0.014	30	0.021	9	0.43	16	0.018	13
0.014	16	0.023	13	0.014	7	0.014	16	0.014	13	0.018	16	0.414	7	0.017	16
0.012	13	0.015	30	0.012	30	0.011	7	0.009	7	0.014	7	0.393	13	0.014	30
0.010	7	0.013	7	0.011	9	0.0055	13	0.009	16	0.013	30	0.390	30	0.014	29
0.010	21	0.010	29	0.007	21	0.0035	9	0.008	21	0.013	13	0.377	19	0.010	21
0.0065	29	0.008	21	0.005	29	0.0017	29	0.007	29	0.007	21	0.33	29	0.009	7
0.0023	9	0.0047	9	0.003	16	0.0006	21	0.0036	9	0.007	21	0.320	9	0.0042	9
ROONEY AND STAPLETON PROCEDURE															
0.063	22	0.019	31	0.048	31	0.015	31	0.025	27	0.014	31	0.492	31	0.033	22
0.004	27	0.014	22	0.026	22	0.011	22	0.012	31	0.010	22	0.481	22	0.0051	27
		0.0073	27	0.014	27	0.006	27	0.008	22	0.008	27	0.382	27		
WILLEMS' METHOD															
0.016	10	0.027	10	0.011	10	0.033	10	0.024	10	0.038	10	0.111	10	0.017	10
SELECTED VALUE															
0.012, $\pm 0.004$		0.013, $\pm 0.005$		0.011, $\pm 0.004$		0.004, $\pm 0.002$		0.010, $\pm 0.004$		0.010, $\pm 0.004$		0.39, $\pm 0.03$		0.014, $\pm 0.005$	

anhydrous methyl alcohol as described by Rooney and Stapleton, and one employed a solution of iodine in absolute alcohol as described by Willems.

The values obtained by the iodine method vary rather widely among themselves. Undoubtedly, inaccurate chemical analysis of the insoluble residue is responsible in part. In studying the data of the eight cooperators who used an aqueous solution of iodine, it was observed that the results obtained by some were consistently high or low, and that the values obtained by cooperators 7, 13, 19, 21 and 29 were generally in good agreement. The "selected values" chosen by the committee from the data of those who used the aqueous solvent are given in Tables 8, 9, 10 and 11. They are based largely on the results of the five cooperators mentioned. It is believed that these selected values are representative of results that may be expected by carefully following the Cunningham and Price procedure.

Because of the limited number of cooperators who used the alcoholic solvents, and the rather wide variation in the values reported, no selected values were chosen for this group. However, a comparison of these values with the selected values is discussed in a later section.

In the following sections there is recorded a brief discussion of the values reported by the eight cooperators who used the aqueous iodine solvent. These cooperators used the Cunningham and Price method except for some small changes by some of the analysts. For example, cooperator 7 used an  $\text{I-FeI}_2$  solution containing approximately 50 grams of iodine and 0.8 gram of ammonium citrate per 100 ml.; cooperator 19 used an  $\text{I-KI}$  solution containing 1 per cent of ammonium citrate, and cooperator 29 used somewhat larger samples (18 to 20 grams).

To facilitate review of the data of Tables 8, 9, 10 and 11, the values are presented graphically in Figs. 3 and 4.

The spread of the results within the selected range may seem rather wide. In general, however, the spread, except for  $\text{FeO}$ , is of about the same order that obtains in the determination of other constituents present in small amounts in ferrous alloys. Furthermore, it should be noted that as regards total oxygen a difference of 0.005 per cent of  $\text{FeO}$  or  $\text{MnO}$ , or 0.002 per cent of  $\text{Al}_2\text{O}_3$  or  $\text{SiO}_2$ , is equivalent to 0.001 per cent of oxygen.

Of the 53 values for the determination of  $\text{Al}_2\text{O}_3$ , received from cooperators who used an aqueous solution of iodine as solvent, 35 are within the selected ranges, 14 above and 4 below. Results reported by cooperators 9 and 27 tend to be high. On the very low-alumina steels, the errors are usually on the high side, probably because of faulty blank corrections. On the other hand, low values were reported by a number of cooperators for the high-alumina steel No. 8, another indication of the tendency toward inaccurate analysis of the insoluble residues. The values obtained by the Rooney and Stapleton procedure (cooperators 22, 27 and 31) are,



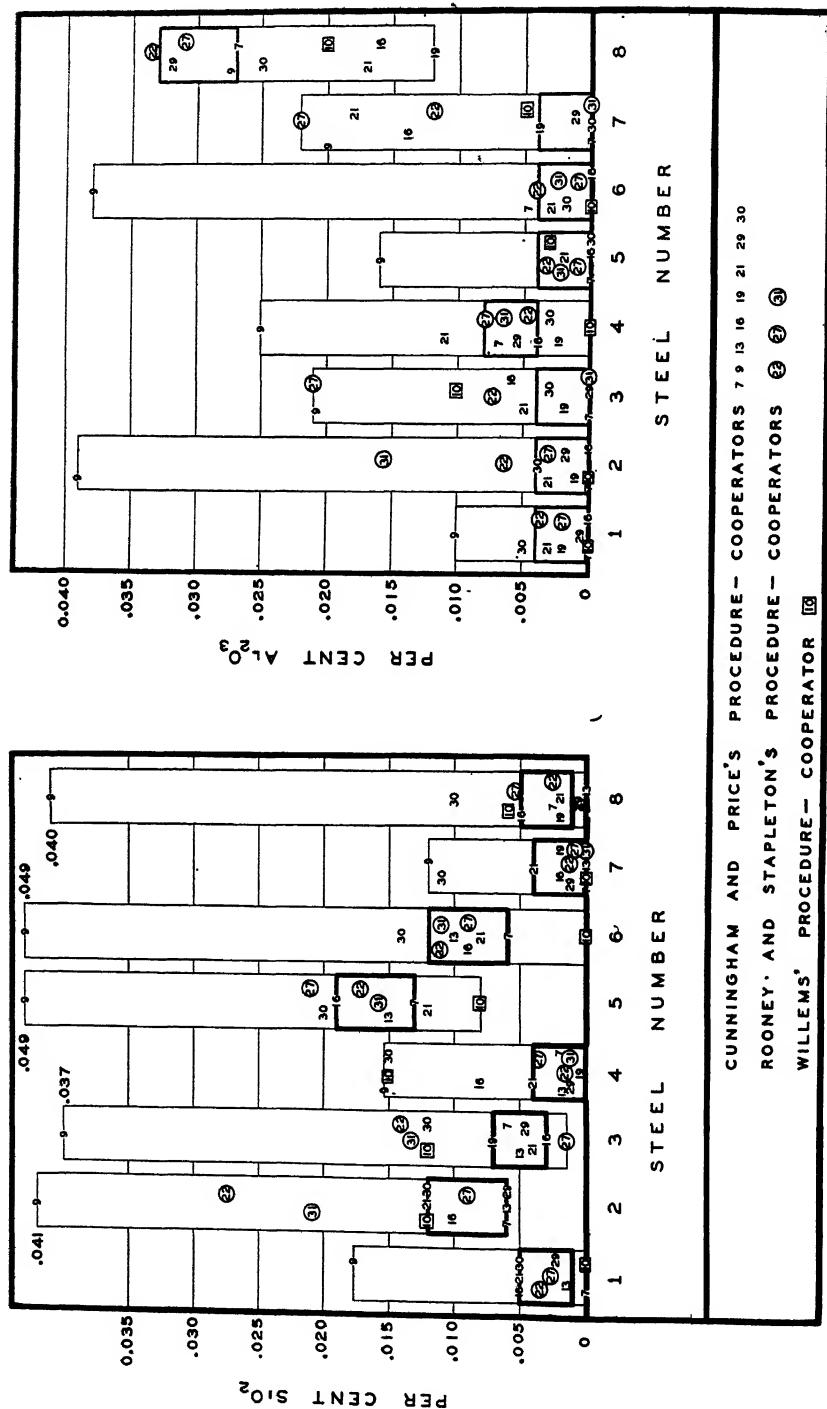


Fig. 3.—Iodine method, determinations of silica and alumina.

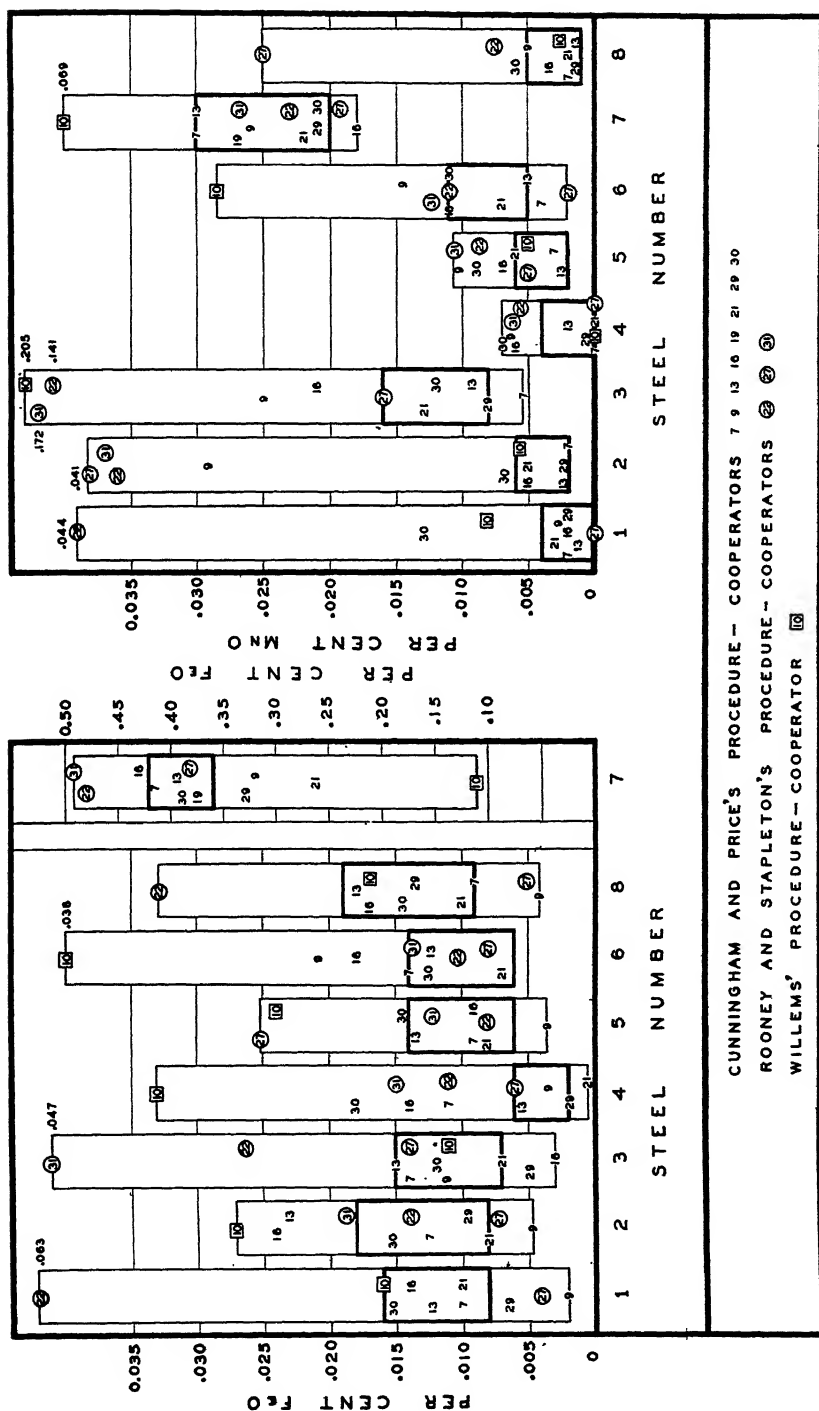


FIG. 4.—IODINE METHOD, DETERMINATIONS OF FERROUS OXIDE AND MANGANOUS OXIDE.

with the exception of steel No. 3, of the same order of magnitude as the selected values.

For the determination of  $\text{SiO}_2$ , 59 values were received from the cooperators who used the aqueous-iodine solvent. Of these, 41 are within the selected range, 15 above and 3 below. Results reported by cooperators 9, 10 and 30 tend to be high. The values obtained by following the Rooney and Stapleton procedure (cooperators 22, 27 and 31) are in general of the same order of magnitude as the selected values except that cooperators 22 and 31 reported appreciably higher values on steels 2 and 3.

For the determination of  $\text{MnO}$ , 56 values were received from the group that employed the aqueous iodine solvent, of which 40 are within the selected range, 13 above and 3 below. The results reported by cooperators 9 and 30 tend to be high. The values obtained by the Rooney and Stapleton procedure vary considerably, and in general are higher than those obtained with the aqueous-iodine solvent. Part of this difference, undoubtedly can be attributed to the fact that  $\text{MnS}$  is not as soluble in the alcoholic solutions as in aqueous iodine solutions and some  $\text{MnS}$  is reported as  $\text{MnO}$ . It is noteworthy that on steel No. 2 the  $\text{MnO}$  values of the alcoholic group are distinctly higher than the selected value, which brings up the question whether or not  $\text{MnO}$  can be quantitatively recovered by the aqueous solvent from a steel of the No. 2 type. On the other hand, the values for  $\text{MnO}$  in iron No. 7 by the aqueous and alcoholic methods are in good agreement. In this iron the maximum possible  $\text{MnO}$  would be 0.031 per cent if the total Mn (0.024 per cent) were calculated to  $\text{MnO}$ .

For the determination of  $\text{FeO}$ , 56 values were received from those who used the aqueous iodine solvent of which 38 are within the selected range, 8 above and 10 below. Results reported by cooperators 9 and 29 tend to be slightly low while those of No. 16 are high. The variation within the selected range is greater for  $\text{FeO}$  than for the other three oxides. This condition naturally complicates the choice of a selected value. The values by the Rooney and Stapleton procedure are slightly higher than the selected values. In general, it appears as though the  $\text{FeO}$  values obtained by the iodine method are somewhat unreliable. For example, with steel No. 4, the selection of 0.004 per cent of  $\text{FeO}$  may be questioned.

#### ACCURACY OF VACUUM-FUSION AND AQUEOUS-IODINE METHODS

These cooperative analyses were undertaken in the hope that the results of different operators would be in sufficiently close agreement to define the value, or a reasonable range of values, that should be obtained by each of the analytical methods. Agreement in the results obtained by different methods, for the same steel, would establish the accuracy of the methods that were in agreement. This hope has not been fully realized up to date. The outstanding feature of these data is the range of results,

i.e., the lack of agreement, in the values obtained by a group of operators using the same method even when each analyst confirms his own results by duplicate or multiple determinations. The information available at present does not suffice to determine whether these discrepancies are primarily the result of inaccuracies in the methods, minor variations in apparatus and procedure of different investigators, or the personal equation.

A selection of representative ranges or "best" values has been possible only for the vacuum-fusion and aqueous-iodine methods as previously described. None of the other methods of analysis are represented by enough concordant results to indicate "best" values, and even in some of the data of the vacuum-fusion and aqueous-iodine methods there is sufficient lack of concordance to render the selection of "best" values difficult and somewhat uncertain. The determination of FeO by the iodine method is a particular illustration of this point.

Direct comparison of the "best" values by the vacuum-fusion and aqueous-iodine methods can be made on the basis of the total oxygen content. This is given directly by the results of the vacuum-fusion analyses and can be computed in the iodine method from the selected values for  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{MnO}$  and  $\text{FeO}$  on the assumption that other combinations of oxygen are not present. This assumption is not strictly correct; the presence of small amounts of other oxides was detected<sup>6</sup> by some of the cooperators, but the amount of oxygen combined in these other oxides may be neglected for present purposes.

Values for total oxygen by the two methods are shown in Table 12. Entirely satisfactory agreement, well within the permissible limits of error for such determinations, is evident for steels 4, 5, 6 and 8. Such duplication of results by two independent methods is regarded as good evidence of the accuracy of both methods, as applied to these samples. The four steels are all of the "killed" type, Nos. 4 and 8 were killed with aluminum, Nos. 5 and 6 with silicon. The iodine method is expected to give its most accurate results on steels of this type, in which the oxygen is present principally as  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$ . The good agreement of the results by the two methods is evidence that appreciable amounts of  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  do not interfere with the satisfactory operation of the vacuum-fusion method.

Steel 2, a silicon-killed steel, with a manganese content of 1.15 per cent, gave a "best value" for total oxygen by the iodine method only half as great as the "best value" by the vacuum-fusion method. In view of the established fact that the presence of manganese frequently causes low recoveries of oxygen to be obtained, the results by the vacuum-fusion

<sup>6</sup> Cooperator 7 reported 0.0013 per cent of  $\text{Cr}_2\text{O}_3$  in steel No. 2, and 0.010 per cent of  $\text{Cr}_2\text{O}_3$  in No. 7. Cooperator 29 reported 0.0015 per cent of  $\text{Cr}_2\text{O}_3$  in steel No. 2; 0.007 per cent of  $\text{Cr}_2\text{O}_3$  and some  $\text{Fe}_2\text{O}_3$  in No. 7, and 0.004 per cent of  $\text{P}_2\text{O}_5$  in steel No. 3. Cooperator 22 reported 0.0026 per cent of  $\text{TiO}_2$  in steel No. 2.

method should not be considered as being too high. It is more probable that the iodine results are low, perhaps because the silicates in this steel are different in composition and more soluble than those in steels 4, 5, 6 and 8. Microscopic studies (cooperators 1, 26 and 33) indicated that the silicate inclusions are larger and more numerous in steel 2 than in steels 5 and 6; in steels 4 and 8 the inclusions are chiefly  $\text{Al}_2\text{O}_3$ .

TABLE 12.—*Comparison of Results by Vacuum-fusion and Aqueous-iodine Methods*

Steel No.	Selected Percentages for Total Oxygen	
	Vacuum-fusion Method <sup>a</sup>	Aqueous-iodine Method <sup>b</sup>
1	0.018	0.006
2	0.017	0.010
3	0.017	0.009
4	0.002	0.005
5	0.009	0.013
6	0.007	0.010
7	0.106	0.095
8	0.017	0.020

<sup>a</sup> Selected values from vacuum-fusion determinations.

<sup>b</sup> Computed from the selected results for  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{MnO}$  and  $\text{FeO}$  obtained by the aqueous-iodine method.

For steels of the "rimming" type, Nos. 1, 3 and 7, the total oxygen by the vacuum-fusion method was appreciably higher than by the iodine method<sup>7</sup>. On the assumption that the vacuum-fusion method yields correct results for killed steels, containing the difficultly reducible oxides,  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$ , it is reasonable to conclude that this method should yield correct results for rimming steels in which the easily reducible oxides,  $\text{FeO}$  and  $\text{MnO}$ , are predominant. It is believed, therefore, that the results obtained by vacuum fusion for steels 1, 3 and 7 are approximately correct and, on the other hand, that the results by the iodine method are somewhat low, perhaps on account of analytical difficulty in determining  $\text{FeO}$  and  $\text{MnO}$  by this method or because of difficulty in the selection of the best values from the reported data for  $\text{FeO}$  and  $\text{MnO}$ . It is not fully apparent why the greatest difference in results by the two methods was obtained for steel 1, unless it was because the  $\text{MnO}$  in this steel is not combined with  $\text{SiO}_2$  and therefore is more readily dissolved than in the other steels.

The evidence of the available data in regard to the accuracy of the two methods may be summarized as follows:

<sup>7</sup> This statement is based on the actual difference and not on the percentage difference in results by the two methods. From the latter standpoint the two methods are in fairly good agreement for iron No. 7.

The accuracy of the vacuum-fusion method for silicon-killed and aluminum-killed steels (Nos. 4, 5, 6 and 8) is demonstrated by agreement with the results of the aqueous-iodine method. The accuracy obtained for killed steels justifies the assumption of accuracy for unkilld steels. A reasonable value was obtained for the oxygen content of steel 2 and indicates that the presence of 1.15 per cent of manganese in a steel does not introduce serious error in the best results obtainable by the vacuum-fusion method.

The accuracy of the iodine method for aluminum-killed steels and for some silicon-killed steels is demonstrated by agreement with the results of the vacuum-fusion method, for steels 4, 5, 6 and 8. The low results obtained for steel 2 indicate that inaccurate results may be obtained on some silicon-killed steels. Low results were obtained on rimming steels. Satisfactory concordance in the results obtained by the iodine method, particularly for FeO, is not yet attainable.

#### THE HYDROGEN-REDUCTION METHOD

The hydrogen-reduction method depends upon the reduction of oxides in the sample by means of purified hydrogen at elevated temperatures. The amount of water vapor in the hydrogen leaving the furnace indicates the amount of oxides reduced. It is generally believed that FeO and MnO are completely reduced under these conditions, but that refractory compounds such as  $Al_2O_3$  and certain silicates are reduced only partially or not at all.

Four of the cooperators in this project reported results obtained by this method. Essential details of apparatus and procedure, according to the reports submitted and the published references (Table 2) are as follows:

COOPERATOR No. 2. The sample of 15 to 30 grams of millings contained in a perforated bucket of Invar was suspended in the center of the vertical furnace tube to avoid contact of hot metals with the quartz tube. The furnace was maintained at  $610^\circ$  to  $620^\circ$  C. for  $1\frac{1}{2}$  hr. to remove "surface oxygen," the gases evolved during this period being discarded. The temperature was then raised to  $1200^\circ$  C. and maintained at this point for 2 hr., for the determination of "contained oxygen." An unusual and outstanding feature of the apparatus was the use of high-frequency induction heating for maintaining the sample at  $1200^\circ$  C. Consequently, the furnace tube was always at a lower temperature than the sample and the possibility of reaction between the quartz tube and the furnace gases thereby reduced. In the analysis of the evolved gases, copper sulphate on pumice was used to remove hydrogen sulphide; oxides of carbon were converted to  $CH_4$  and  $H_2O$  by means of a nickel catalyst maintained at  $260^\circ$  to  $275^\circ$  C.; water vapor was absorbed in  $P_2O_5$ ; the blank correction did not exceed 0.002 per cent of oxygen.

COOPERATOR No. 5. A 10-gram solid sample was placed in an alundum boat together with 25 grams of a 1:1 alloy of tin and antimony and maintained for 1 hr. at 1080° C. A nickel catalyst was used to decompose oxides of carbon; water was absorbed in  $P_2O_5$ ; the blank correction was consistently 0.002 per cent of oxygen. Complete details of the apparatus and procedure are not available.

COOPERATOR No. 17. A 25-gram solid sample was placed in a porcelain boat together with an equal weight of antimony and heated for 2 hr. at 1200° C. Copper sulphate on pumice was used to remove sulphur compounds from the gases; a nickel catalyst was used; water was absorbed in phosphorus pentoxide.

COOPERATOR No. 32. Sample consisted of a polished cylinder. A modified form of Oberhoffer's apparatus was used with the reduction temperature maintained at 1200° to 1250° C. Iodine pentoxide was used to oxidize CO in the evolved gases.

TABLE 13.—*Determinations of Oxygen by Hydrogen-reduction Methods*

Oxygen, Per Cent								
Steel No..	1	2	3	4	5	6	7	8
CHIP SAMPLE; NOT MELTED								
Cooper- ator 2....	0.024	0.027	0.027	0.008	0.022	0.010	0.076	0.015
SAMPLE MELTED WITH ANTIMONY OR ANTIMONY AND TIN								
5....	0.020	0.020	0.025	0.012	0.016	0.010	0.106	0.023
17....	0.019	0.0077	0.018	0.0077	0.0013	0.0028	0.098	0.0028
32....	0.021	0.012	0.021	0.0005	0.0078	0.0043	0.100	0.020

The results reported by these four cooperators are shown in Table 13. The data are too few and the concordance of results is not sufficiently close to permit a selection of representative values for the hydrogen-reduction method. For each steel, the four determinations extend over a considerable range, frequently greater than that of the 15 determinations by the vacuum-fusion method. The data are shown graphically in Fig. 5. The range of acceptable values for the total oxygen content of each steel, according to the vacuum-fusion method, is indicated by a heavily outlined box in each grouping.

It is evident from Fig. 5 that the results of cooperator 32 are consistently near to or within the limits of acceptable values established for the vacuum-fusion method. Although the results of the other cooperators sometimes fall within the acceptable ranges, the results of cooperators 2

and 5 are usually higher and those of cooperator 17 frequently lower than the acceptable values for the vacuum-fusion method.

Available information is not sufficient to explain the lack of agreement between the results of different investigators or between the results by the hydrogen-reduction and vacuum-fusion methods. The hydrogen-reduction method is generally assumed to recover only the oxygen present as

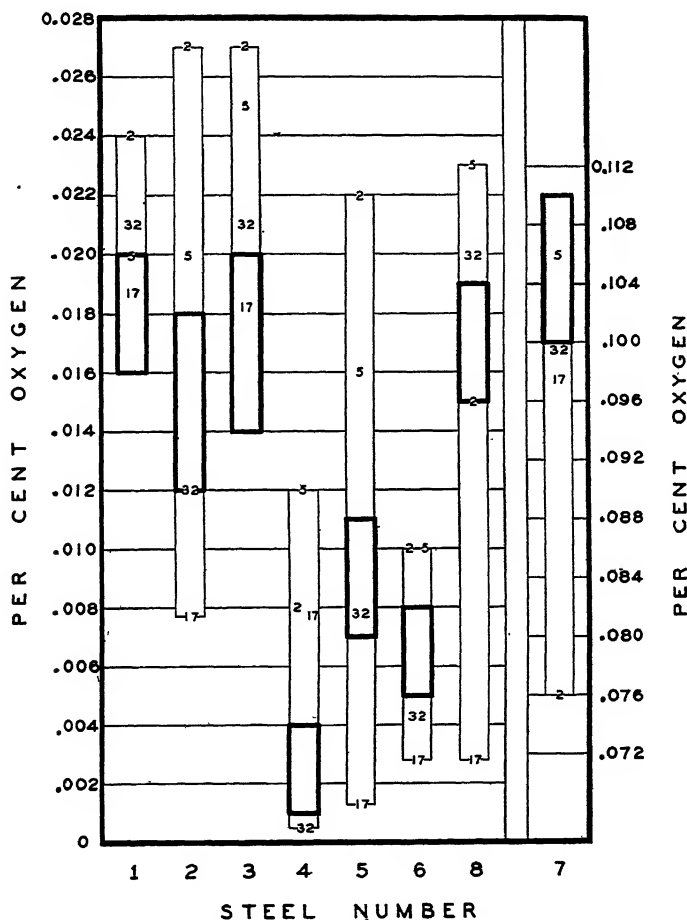


FIG. 5.—HYDROGEN-REDUCTION METHOD, DETERMINATION OF OXYGEN.

FeO or MnO, but for steel 8, in which the oxygen is present chiefly as  $\text{Al}_2\text{O}_3$ , three of the four results are as high as the results by the vacuum-fusion method. On the other hand, for the sample of open-hearth iron in which the oxygen is present chiefly as FeO and MnO, the results tend to run lower than those by vacuum fusion. The best agreement within the results by the hydrogen-reduction method was obtained for steel 1, and for this steel the results by hydrogen reduction and vacuum-fusion are in



good agreement, whereas those by iodine and vacuum fusion are not. More data, and particularly more concordant data, are needed to establish the accuracy of the hydrogen-reduction method.

### THE ELECTROLYTIC METHOD

In this method the sample is the anode in an electrolytic cell. The composition of the electrolyte and the conditions of electrolysis are controlled in order that the soluble metallic constituents may be separated from the insoluble nonmetallic material. At the end of the electrolysis the loss in weight of the anode is determined and the insoluble residue is collected and analyzed. Several electrolytes have been proposed, for each of which advantages have been claimed. Four were employed in the present cooperative analyses, as follows:

G. R. Fitterer and coworkers used an aqueous solution containing 3 per cent of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and 1 per cent of  $\text{NaCl}$ .  $\text{MnO}$ ,  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  were determined in the insoluble residue. Basic ferric sulphate and ferrous hydroxide precipitate during electrolysis of this solution and contaminate the residue so that the  $\text{FeO}$  content of the sample cannot be determined.

F. W. Scott recommended an aqueous electrolyte containing approximately 45 grams of magnesium iodide and 2 grams of iodine per liter and claimed that iron dissolves without hydrolysis in this electrolyte, and that the sulphides, phosphides and carbides that exist in steel are completely decomposed.  $\text{FeO}$  and  $\text{MnO}$ , as well as  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$ , are determined in the insoluble residue.

H. Styri found that  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  could be conveniently determined in an electrolyte consisting of a 3 per cent aqueous solution of ferrous chloride. In some experiments a solution containing 3 per cent of sodium citrate and 0.1 per cent of ferrous chloride was used in the anode compartment.  $\text{FeO}$  and  $\text{MnO}$  were not determined in these experiments.

Benedicks' electrolyte for the anode compartment consisted of 0.1 N potassium bromide solution containing about 10 per cent of sodium citrate. The cathode compartment contained a 10 per cent solution of a copper salt, either sulphate or bromide. The published description of this electrolyte stated that the determination of  $\text{FeO}$ ,  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  was adequate but that the determination of  $\text{MnO}$  was not quite satisfactory.

Six of the cooperators reported results by electrolytic methods, as shown in Table 14. Scott's electrolyte and Benedicks' electrolyte were used for the determination of all four of the constituents,  $\text{FeO}$ ,  $\text{MnO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ .  $\text{FeO}$  was not determined by those using Fitterer's electrolyte, and Styri's electrolyte was used only for the determination of  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$ . Two cooperators heat-treated the samples before electrolysis to see if heat-treatment and the resulting redistribution of carbides affected the determination of  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$ .

TABLE 14.—Results Obtained by Electrolytic Methods

Steel No.....	1	2	3	4	5	6	7	8
Determinations of Silica, Per Cent								
Fitterer's electrolyte:								
Cooperator: 3....	0.005	0.070	0.008	0.006	0.024	0.081	0.006	0.006
3H <sup>a</sup> ..	0.011	0.054 <sup>b</sup>	0.010	0.004	0.017	0.014	0.004	0.007
19....	0.004	0.021	0.020	0.002	0.016	0.018	0.002	0.003
30....	0.001	0.014	0.0045	0.001	0.027	0.042	0.0015	0.0015
Scott's electrolyte:								
Cooperator: 4....	0.001	0.010	0.003	0.0004	0.013	0.007	0.0008	0.004
20....	0.003			0.004	0.024	0.013	0.009	0.010
Styri's electrolyte:								
Cooperator: 12....	0.003	0.047	0.004	0.0045	0.0055	0.046	0.004	0.004
12H <sup>a</sup> ..		0.051		0.0065		0.07		0.007
Benedicks' electrolyte:								
Cooperator 20....	0.020	0.079	0.027	0.024	0.076	0.140	0.092	0.013
Determinations of Alumina, Per Cent								
Fitterer's electrolyte:								
Cooperator: 3....	0.002	0.009	0.004	0.025	0.002	0.002	0.006	0.016
3H <sup>a</sup> ..	nil	0.002	0.003	0.024	0.002	0.004	0.005	0.024
30....	0.0007	0.0007	0.0003	0.003	0.001	0.002	0.0004	0.013
Scott's electrolyte:								
Cooperator: 4....	0.004	nil	nil	0.006	nil	nil	0.004	0.035
20....	0.004			0.009	0.005	0.007	0.010	0.042
Styri's electrolyte (fer-								
rous chloride):								
Cooperator: 12....	0.001	0.005	0.002	0.032	0.0015	0.003	0.003	0.021
12H <sup>a</sup> ..	0.0015	0.004	0.003	0.022	0.002	0.003	0.003	0.025
Benedicks' electrolyte:								
Cooperator 20....	0.005	0.013	0.006	0.012	0.006	0.009	0.009	0.070
Determinations of Ferrous Oxide, Per Cent								
Fitterer's electrolyte:								
FeO not reported....								
Scott's electrolyte:								
Cooperator: 4....	0.020	0.009	0.075	0.012	0.015	0.008	0.421	0.004
20....	0.185 <sup>d</sup>	0.016 <sup>d</sup>	0.515 <sup>d</sup>	0.080 <sup>d</sup>	0.052 <sup>d</sup>	0.094 <sup>d</sup>	0.480 <sup>d</sup>	0.195 <sup>d</sup>
Styri's electrolyte: FeO								
not reported .....								
Benedicks' electrolyte:								
Cooperator 20....	0.091 <sup>d</sup>	0.073 <sup>d</sup>	0.047 <sup>d</sup>	0.040 <sup>d</sup>	0.040 <sup>d</sup>	0.029 <sup>d</sup>	0.347 <sup>d</sup>	0.220 <sup>d</sup>
Determinations of Manganous Oxide, Per Cent								
Fitterer's electrolyte:								
Cooperator: 3....	-0.001 <sup>e</sup>	nil	-0.021 <sup>e</sup>	0.012	0.009	0.079	0.028	0.103
3H <sup>a</sup> ..	0.014	0.017	0.080	0.017	0.019	0.041	0.018	0.030
19....	0.029	0.097	0.041	0.030	0.053		0.019	0.065
30....	0.018	0.102	0.055	0.083	0.049	0.051	nil	0.052
Scott's electrolyte:								
Cooperator: 4....	0.006	0.033	0.074	0.007	0.007	0.0035	0.0235	0.009
20....	0.001 <sup>d</sup>	0.001 <sup>d</sup>	0.004 <sup>d</sup>	0.001 <sup>d</sup>	0.002 <sup>d</sup>	0.001 <sup>d</sup>	0.022 <sup>d</sup>	0.004 <sup>d</sup>
Styri's electrolyte: MnO								
not reported .....								
Benedicks' electrolyte:								
Cooperator 20....	0.013 <sup>d</sup>	0.073 <sup>d</sup>	0.184 <sup>d</sup>	0.008 <sup>d</sup>	0.014 <sup>d</sup>	0.016 <sup>d</sup>	0.019 <sup>d</sup>	0.023 <sup>d</sup>

<sup>a</sup> Cooperator 3 determined MnO, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> in samples as received (3) and after heat-treatment (3H). For determinations of SiO<sub>2</sub> the samples were annealed for 18 hr. at 650° C.; for MnO the samples were held at 1000° C. for 12 hr. and quenched in water.

<sup>b</sup> After a second annealing of steel 2 at 675° C. for 18 hr., the value obtained for SiO<sub>2</sub> was 0.018 per cent.

<sup>c</sup> Cooperator 12 studied the effect of heat-treatment on the determination of Al<sub>2</sub>O<sub>3</sub>. "Soft" samples (12) were in the as-received condition; "hard" samples (12H) were quenched from 1100° C. in saturated brine.

<sup>d</sup> Including sulphides.

<sup>e</sup> Negative values for MnO indicate discrepancies in the separation of MnO and MnS.

The comparison of results obtained by different observers using the same electrolyte is frequently complicated by variations in methods of analysis and other departures for uniform procedure. There are not

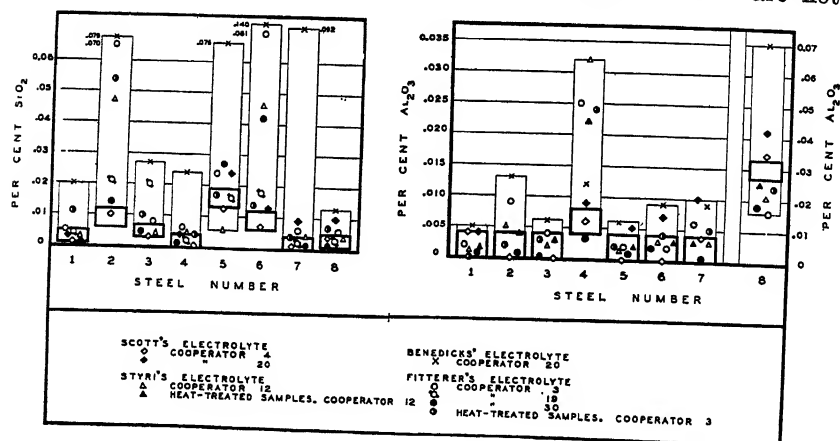


FIG. 6.—ELECTROLYTIC METHOD, DETERMINATIONS OF SILICA AND ALUMINA.

enough data available to justify the selection of "best" values for any one electrolyte or for the electrolytic procedure in general. However, the

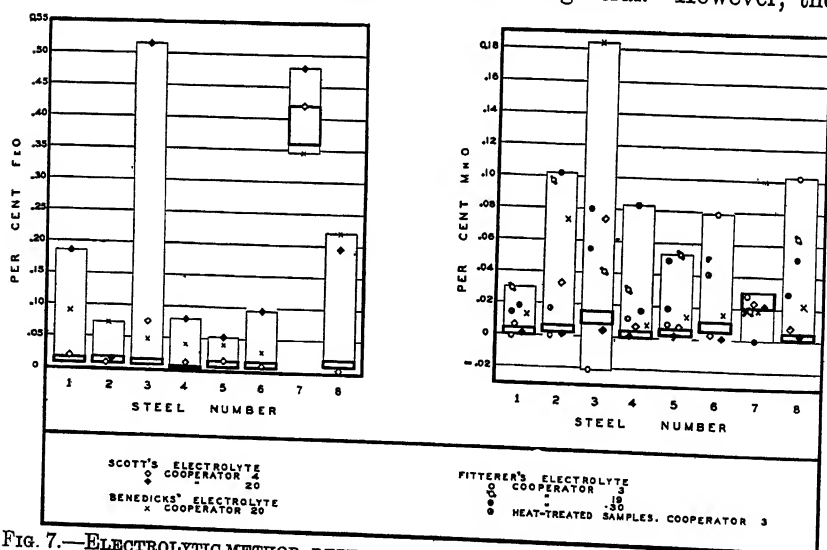


FIG. 7.—ELECTROLYTIC METHOD, DETERMINATIONS OF FERROUS OXIDE AND MANGANOUS OXIDE.

results obtained by electrolytic methods can be compared with the selected values by the iodine method, as shown in Figs. 6 and 7.

Electrolytic methods, in general, are believed to be more reliable for the determination of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  than for  $\text{FeO}$  and  $\text{MnO}$ . The latter

determinations are complicated by the presence of carbides and sulphides in the insoluble residue; by the presence of hydrated compounds formed by anodic oxidation of metallic constituents during the solution process; and by the presence of small metallic particles from mechanical disintegration of the anode. The consistently high results for FeO and MnO, by electrolytic methods, as compared with the selected values by the aqueous-iodine method (indicated by the heavily outlined boxes in Fig. 7) may reflect the analytical difficulties in the determination of FeO and MnO, rather than a consistent difference in the two methods in separating FeO and MnO from the rest of the sample. The values by the iodine method are believed to be approximately correct for steels 4, 5, 6 and 8, but are low for steels 1, 2, 3 and 7. Consequently, if the electrolytic determinations of FeO and MnO are accurate, they should coincide with the results for steels 4, 5, 6 and 8 and should be higher than the results for steels 1, 2, 3 and 7. This is not true; for each steel the electrolytic values are scatteringly higher than those by the iodine method by about the same amount.

Fig. 6 shows that there is somewhat better agreement between results by the two methods, in the determination of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  than of FeO and MnO. However, even in the determination of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ , there is a decided lack of concordance in results obtained by electrolytic methods.

In comparison with the selected values for the iodine method the results of cooperator 4, using Scott's electrolyte, are the best. His determinations varied somewhat from the published procedure (see reference, Table 2, cooperator 4) particularly in the treatment of the residue to remove sulphides and metallic particles prior to analysis. After washing with KI solution, the residue from the electrolysis was treated with a 12 per cent solution of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (previously neutralized with MgO), filtered, and the residue digested with 25 per cent sodium citrate solution. It was then filtered, washed with 2 per cent ammonium citrate solution and thereafter was treated as described in the published article. His results for  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  are invariably within or very near the range of the iodine values; his determinations of FeO are in good agreement with the iodine values except for the high-sulphur steel, No. 3; his values for MnO are in good agreement with the iodine values except for steels 2 and 3, for which the iodine values are believed to be low. This electrolyte also was used by cooperator 20. The latter's results for  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  sometimes are higher than the results of cooperator 4 but in general are in good agreement with them. In reporting, cooperator 20 suggested that the results obtained for  $\text{SiO}_2$  may be somewhat high on account of solubility of glass during the prolonged electrolysis. It was also stated that when Scott's electrolyte was used the sulphides and phosphides of manganese were strongly decomposed but the corresponding compounds

of iron were only partly decomposed. Furthermore the residue often contained appreciable amounts of fine-grained, undecomposed metallic ingredients. These factors combine to yield erroneously high results for FeO and to a less pronounced extent for MnO.

Cooperator 20 also used Benedicks' electrolyte and considered it promising. Comparison of his results obtained with Benedicks' and Scott's electrolytes shows that consistently higher results for  $\text{Al}_2\text{O}_3$  and decidedly higher results for  $\text{SiO}_2$  were obtained with Benedicks' electrolyte. Contamination by sulphides, as reported by cooperator 20, seems to have had somewhat less effect on the FeO determinations, and more effect on the MnO determinations, than when Scott's electrolyte was used.

The results obtained by the three cooperators who used Fitterer's electrolyte vary considerably in some of the determinations of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  and in most of the determinations of MnO. Cooperator 3 reported that previous work (unpublished) with steels containing 0.60 to 0.80 per cent of carbon indicated that the annealing temperature had a tremendous effect on the percentage of silica found. Accordingly, samples of the eight steels were run in the as-received condition and after annealing for at least 12 hr. at  $650^\circ\text{C}$ . The data in Table 14 show that this treatment affected the silica results only for two steels, Nos. 2 and 6, with carbon contents in excess of 0.4 per cent; did not appreciably affect the results for alumina; improved the results for MnO, by bringing them into better agreement with those of other cooperators for the samples that were not heat-treated. Cooperator 3 expressed the opinion that "the electrolytic method must be considerably modified if steels above about 0.35 per cent carbon are investigated. There is also the possibility that the results on lower carbon steels might be affected by the heat-treatment."

Styri's electrolyte was used by cooperator 12 for the determination of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  and to observe the effect on these determinations of the changes in structure that occurred on quenching the samples from  $1100^\circ\text{C}$ . in brine. The data indicate that this quenching had no marked effect on the results for silica and alumina. For the samples as received, the determinations of silica yielded good results for five of the steels, high results for steels 2 and 6, and somewhat low results for steel 5. Reasonable values for alumina likewise were obtained except for steel 4. Cooperator 12 expressed the opinion that some of the results for alumina were probably high because of contamination of the residue.

More data are needed to establish the accuracy of the electrolytic method. One of the items to be studied further is the question of anodic oxidation. Cooperator 20 observed the formation of pentabromacetone at the anode during electrolysis and considered this a possible source of anodic oxidation of the sample.

## MISCELLANEOUS METHODS

Reports of the results of microscopic examination were submitted by three cooperators: a "cleanness rating" of the eight steels, based on an inclusion count according to Epstein's method, was prepared by cooperator 1; cooperators 26 and 23 made extended microscopic studies. This microscopic evidence on sulphide, duplex and oxide inclusions, as well as structural and unusual features, has not been of particular value in the quantitative determination of the oxygen content of these steels.

TABLE 15.—Results Obtained by the Mercuric Chloride, Chlorine, Fractional Vacuum-fusion, Nitric Acid and Hydrochloric Acid Methods

Steel No.			1	2	3	4	5	6	7	8
Deter- mina- tion	Method	Coop- erator No.								
SiO <sub>2</sub> , Per Cent	Chlorine.....	15	0.001	0.015	0.016	0.001	0.016	0.008	0.001	0.004
		17	0.001	0.096	0.012	0.003	0.019	0.007	0.005	0.009
		20	0.003	0.025	0.020	0.012	0.019	0.015	0.004	0.011
	Fractional vacuum-fusion	24	0.003	0.011	0.007	0.002	0.013	0.004	0.0055	0.017
	Nitric acid.....	9	0.008	0.0015	0.011	0.011	0.014	0.007	0.011	0.013
	Hydrochloric acid.....	29	0.001	0.001	0.001	<0.001	0.012	0.002	<0.001	0.001
Al <sub>2</sub> O <sub>3</sub> , Per Cent	Chlorine.....	15				0.002				0.024
		17	0.0	0.004	0.001	0.003	<0.001	0.001	0.001	0.008
		20	0.006	0.012	0.003	0.003	0.003	0.005	0.023	0.042
	Fractional vacuum-fusion	24	0.0075	0.002	0.0095	0.0035	0.002	0.002	0.000	0.0095
	Nitric acid.....	9	0.001	<0.001	<0.001	0.0015	<0.001	0.002	0.003	0.027
		13			nil	0.0055			0.002	0.033
	Hydrochloric acid.....	13							0.002	
		29	<0.001	<0.001	<0.001	0.0035	0.001	0.001	0.0015	0.030
						0.0055*			0.007*	0.035*
FeO, Per Cent	Mercuric chloride.....	20	0.290	0.038	0.284	0.061	0.068	0.043	0.630	0.288
		25	0.313	0.135	0.323	0.316	0.115	0.135	0.720	0.472
	Chlorine.....	17	0.001	0.013	0.005	0.002	0.007	0.019	0.068	0.023
		20	0.013	0.035	0.040	0.040	0.034	0.037	0.187	0.024
	Fractional vacuum-fusion	24	0.009	0.0045	0.007	0.000	0.000	0.000	0.449 <sup>b</sup>	0.000
	Nitric acid.....	9	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
MnO, Per Cent	Mercuric chloride.....	20	0.004	0.004	0.012	0.004	0.006	0.004	0.050	0.005
		25	0.0015	0.0025	0.010	<0.001	<0.001	0.0015	0.012	<0.001
	Chlorine.....	17	<0.001	0.025	0.005	0.007	0.0075	0.011	0.0035	0.011
	Fractional vacuum-fusion	24	0.058	0.027	0.049	0.000	0.018	0.013	<sup>b</sup>	0.009
	Nitric acid.....	9	<0.001	<0.001	0.003	<0.001	0.001	0.000	<0.001	0.001

\* In a modification of the hydrochloric acid method the remaining weight of the residue, after volatilizing the silica, was assumed to be Al<sub>2</sub>O<sub>3</sub>. This modified procedure should not appreciably affect the results for SiO<sub>2</sub> but gives high results for Al<sub>2</sub>O<sub>3</sub>, if the residue contains Fe<sub>2</sub>O<sub>3</sub> or compounds such as aluminum silicates, which are not decomposed by hydrofluoric acid.

<sup>b</sup> In iron 7, FeO and MnO were determined together and reported as FeO.

Few data are available on the oxide content of the eight steels according to the mercuric chloride, chlorine, fractional vacuum-fusion, nitric acid, and hydrochloric acid methods (Table 15). In view of the limited

number of data available for each of these methods, the most practical comparison is with the selected values for the iodine method, indicated by the heavily outlined areas in Figs. 8 and 9.

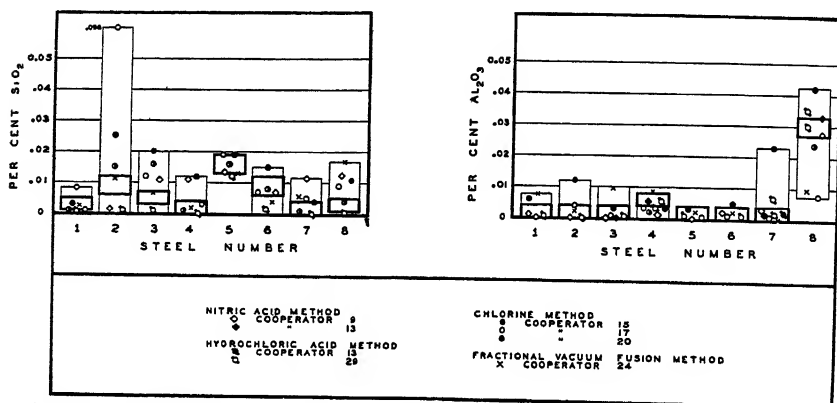


FIG. 8.—MISCELLANEOUS METHODS, DETERMINATIONS OF SILICA AND ALUMINA.

### *The Mercuric Chloride Method*

In the mercuric chloride method, the sample is subjected to the action of an aqueous solution of mercuric chloride, 120 grams per liter, in the

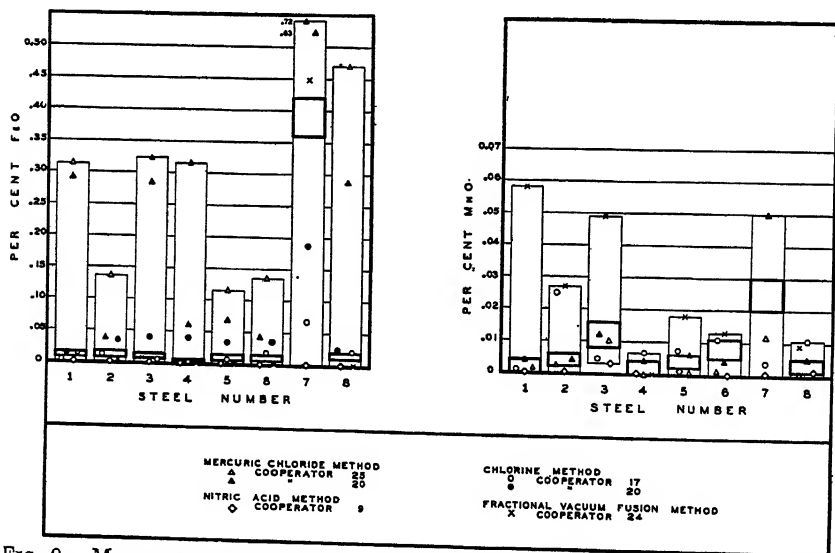


FIG. 9.—MISCELLANEOUS METHODS, DETERMINATIONS OF FERROUS OXIDE AND MANGANOUS OXIDE.

absence of air, until the reaction  $\text{Fe} + 2\text{HgCl}_2 = \text{FeCl}_2 + 2\text{HgCl}$  is complete.  $\text{FeO}$  and  $\text{MnO}$  remain in the insoluble residue. Compounds of manganese and iron with phosphorus, sulphur and nitrogen are not

decomposed quantitatively. The presence in the insoluble residue of these compounds, or of metallic particles from incomplete decomposition of the sample, leads to high results for FeO and MnO. The determination of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  is not attempted.

Two cooperators, Nos. 20 and 25, used the mercuric chloride method for the determination of FeO and MnO in the eight steels. Fig. 9 shows that the results for FeO are consistently higher than those obtained by any other method. High contents of phosphorus and sulphur might account for the high values for FeO in steel 3, but the equally high values obtained for other steels, with lower P and S contents, indicate contamination of the residue by particles of metal. The results of the two cooperators for MnO are in good agreement except for iron 7. Furthermore, the results for MnO obtained by the mercuric chloride method are usually in agreement with the selected results by other methods. The good results obtained for MnO, even in steel 3, further indicate that incomplete solution of the sample, resulting in the presence of metallic particles in the residue, is perhaps a more serious source of error than the presence of phosphide and sulphide compounds.

#### *The Chlorine Method*

In this method of analysis the sample is heated several hours at a moderate temperature in a stream of purified chlorine. The metallic constituents of the sample are thereby converted to chlorides, which are largely volatile under these conditions. The oxide constituents are not attacked by the chlorine and are determined by suitable means in the residue from the chlorination treatment.

Cooperator 17 chlorinated the samples at 500° C. and determined  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , FeO and MnO in the residue. Cooperator 20 chlorinated the samples at 350° C. and determined  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and FeO. Cooperator 15 determined  $\text{SiO}_2$  in all the steels and  $\text{Al}_2\text{O}_3$  in two steels, by chlorinating at about 380° C.

Fig. 8 shows that approximately half of the results for  $\text{SiO}_2$ , by the chlorine method, are in good agreement with those by the iodine method, and the results for  $\text{Al}_2\text{O}_3$  also are usually in reasonable agreement, although occasional high and low values were obtained. In the determination of FeO (Fig. 9) the results of cooperator 20 are consistently higher than those of cooperator 17. The latter's results are consistently in good agreement with results by the iodine method. This suggests that chlorination at 350° C. (cooperator 20) yields too high results for FeO, perhaps because of contamination of the residue by particles of undecomposed sample. Both cooperators reported low values for the FeO content of iron 7. Determinations of MnO by the chlorine method were made only by cooperator 17 and these determinations (Fig. 9) are not in consistent agreement with the results obtained by any of the other methods.



### *The Fractional Vacuum-fusion Method*

This modification of the vacuum-fusion method is based on the assumption that the oxides in a steel can be separated according to the temperatures necessary for their reduction. The FeO in a steel can be completely reduced at 1050° C., whereas temperatures of 1170°, 1320°, and 1570° C., respectively, are necessary for the reduction of MnO, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>. The sample, to which tin has been added to lower the melting point, is maintained at each of these temperatures successively, and the amount of gas evolved at each is used to indicate the amount of one of the oxide constituents.

Only one set of results (cooperator 24) is available. Fig. 8 shows that the results for SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> are generally in good agreement with the selected values by the iodine method. For steels 7 and 8 somewhat high results for SiO<sub>2</sub> are compensated by low results for Al<sub>2</sub>O<sub>3</sub>, which indicates faulty separation of the two fractions in these two determinations. The values for FeO obtained in the fractional vacuum-fusion method are in good agreement with, or somewhat lower than, the iodine results. The high value for FeO in iron 7 represents the sum of the FeO and MnO, as the two constituents apparently were not separated in this determination. The MnO values indicated by the fractional vacuum-fusion analyses are consistently higher, sometimes appreciably so, than the values obtained by other methods. These high values for MnO by the fractional vacuum-fusion method, particularly for steels 1, 2 and 3, perhaps explain the low recoveries of oxygen by the iodine method, as compared with the results by vacuum fusion. However, determinations by one observer cannot be unreservedly accepted, according to the evidence of the data assembled in these cooperative analyses. Further information is needed to establish the accuracy of the fractional separations and the reproducibility of results by the fractional method in the hands of different operators. In the previous discussion of the vacuum-fusion method, the values for total oxygen obtained by the fractional method were compared with the selected values for the regular vacuum-fusion method. For five of the eight steels the fractional method yielded satisfactory values for total oxygen, but for the other three steels high results were obtained.

### *The Nitric Acid Method*

This method depends upon the solubility of metallic constituents and the relative insolubility of oxides, particularly alumina, in approximately 10 per cent nitric acid.

Fig. 9 shows that cooperators 9 and 13 obtained results for Al<sub>2</sub>O<sub>3</sub> that are in excellent agreement with selected results by the other methods. The determination of SiO<sub>2</sub> was less satisfactory than that of Al<sub>2</sub>O<sub>3</sub>, the results for SiO<sub>2</sub> being too high unless the hydrated silicic acid, formed

during the solution of metallic silicon, was completely separated, from the  $\text{SiO}_2$  and silicate inclusions in the residue. On the other hand, low results for  $\text{SiO}_2$  may be caused by partial solubility in the acid medium of some of the silicates that may occur in steel. The high results for  $\text{SiO}_2$ , reported by cooperator 9 for five of the steels, indicate contamination of these residues by hydrated silicic acid. Determinations of  $\text{FeO}$  and  $\text{MnO}$  by the nitric acid method, made by cooperator 9, illustrate the accepted belief that the method is not applicable to these determinations. The results (Fig. 9) demonstrate the almost complete solubility, in nitric acid, of  $\text{FeO}$  and  $\text{MnO}$  as they exist in these eight steels.

### *The Hydrochloric Acid Method*

In this method diluted hydrochloric acid, approximately two volumes of water to one of concentrated acid, is employed to separate the metallic from the oxide constituents.  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  are determined in the insoluble residue. The method is not applicable to the determination of  $\text{FeO}$  and  $\text{MnO}$ , owing to the solubility of these in the acid medium.

The data (Table 15 and Fig. 8) show that results for alumina by this method are in excellent agreement with those by the iodine method. The determination of  $\text{SiO}_2$  by the hydrochloric acid method, as in the nitric acid method, is affected by the partial solubility of certain silicates and by the presence of hydrated silicic acid. The consistently low results for  $\text{SiO}_2$ , obtained by cooperator 29, indicate that these determinations were more affected by the solubility of the silicates than by the presence of hydrated silicic acid.

### AUTHORS' COMMENTS

The first impression derived from a study of the data of these cooperative analyses usually is that the results as a whole are decidedly unsatisfactory and indicate that none of the methods for determining oxygen or oxides is sufficiently accurate to conform to the requirements of modern metallurgical analysis. This impression is based on the assumption that chemical analysis is equally accurate for large and small amounts, whereas actually this assumption is decidedly erroneous. The accurate determination of very small amounts, thousandths or even hundredths of one per cent, is a separate field in analytical procedure. Even the standardized methods of chemical analysis, for the determination of common elements such as carbon, silicon, sulphur and manganese, are less accurate for very small amounts than for larger amounts. In the preparation of Standard Samples at the National Bureau of Standards the lack of agreement in the results obtained by skilled analysts in determinations of small amounts of common elements is at times disturbing to one's inherent belief in the accuracy of chemical analysis.

These considerations indicate that the data of the cooperative analyses are fairly satisfactory. In fact, some of the results compare favorably with those obtained in determinations of corresponding amounts of the common constituents of ferrous materials.

Of the two methods of analysis for which the largest number of data are available, the results of the vacuum-fusion method are in better agreement among themselves than are those obtained by the aqueous-iodine method. However, in consideration of the data obtained by the latter method further allowance should be made for the complicated procedure and the number of operations that must be performed in one analysis. The approximate magnitude of the best results by the vacuum-fusion method is clearly indicated by the data for each steel. Some of the selected values for the aqueous-iodine method likewise are clearly indicated by concordant results, but in other determinations the lack of concordant data introduces an element of uncertainty in the selection of best values. The upper and lower limits of the acceptable ranges, to include permissible variations from the selected values, represent the considered opinion of the reviewing committee. It is recognized that there may be differences in opinion as to the proper location of some of the acceptable ranges. Raising or lowering the range as a whole, by one or two thousandths of one per cent, in several cases would appreciably affect the number of cooperators who obtained acceptable results by the vacuum-fusion method.

The conclusions derived from detailed consideration of the cooperative data may be summarized, as follows:

The vacuum-fusion method yields accurate results for all eight of the steels. We believe that the best results obtained by this method are close approximations of the true oxygen contents of each of the steels. Recommendations have been made in regard to the procedure and apparatus to be employed in order that the best results may be obtained.  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ , as they occur in these steels, are completely reduced in the vacuum-fusion procedure; the error resulting from interference of manganese, at least up to 1 per cent of manganese, is not so serious with the recommended form of apparatus as it was formerly considered to be. The chief cause of erratic results appears to be spattering of the sample, during melting or shortly thereafter. A convenient and reliable means of avoiding this source of error is not yet available.

The aqueous-iodine method yields accurate results for aluminum-killed steels and for some silicon-killed steels, but for others, especially steels of the rimming type, low results are obtained. The data for steels 1, 2 and 3, and to a lesser extent for iron 7, show clearly that the aqueous-iodine method cannot be relied upon for determining the total oxygen content of all steels. Part of the discrepancy may be due to the fact that some of the oxygen is present in the form of dissolved or

entrained gases that are not recoverable by residue methods. Further efforts in standardization of the method, down to minute details of procedure, undoubtedly will result in improved agreement in the results obtained by different analysts. Further study of the determinations of FeO and MnO is particularly needed and the need for greater accuracy in the chemical analysis of the small amounts of insoluble material obtained in the residue methods is to be emphasized.

None of the other methods is represented by sufficiently concordant data to justify the drawing of definite conclusions. The hydrogen-reduction method yields results of the same order of magnitude as the vacuum-fusion results, but further work to standardize the procedure of the hydrogen-reduction method is necessary. Likewise, the results of the other residue methods are of the same order of magnitude as the results obtained by the aqueous-iodine method and are more accurate for the determination of  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  than for FeO and MnO. Further standardization of the methods is desirable.

The hope entertained at the beginning of this cooperative analysis, that the results obtained would define the accuracy and limits of usefulness of methods employed for the determination of oxygen and oxides in steel, has not been completely realized. Valuable information has been obtained in regard to the accuracy of the vacuum-fusion and aqueous-iodine methods, but for the other methods there is obvious need of further standardization before their accuracy can be determined. The continuation or extension of this program of cooperative analyses apparently should be postponed until the various methods of analysis have been better standardized.

The sponsors of the project are deeply appreciative of the time and effort expended by the cooperators; the authors are sincerely grateful to Dr. Chipman and the reviewing committee for invaluable assistance in the difficult task of reviewing the data.

#### APPENDIX

Subsequent to the compilation of this report, additional data have been received as follows:

F. W. Scott (cooperator 4) obtained results from additional determinations on steel 3 as shown in Table 16. His comment on these new

TABLE 16.—*Additional Determinations on Steel 3*

Weight of Sample, Grams	$\text{SiO}_2$ , Per Cent	MnO, Per Cent	FeO, Per Cent	$\text{Al}_2\text{O}_3$ , Per Cent	Calculated Oxygen, Per Cent
107.7	0.0020	0.115	0.0048	nil	0.028
100.9	0.0023	0.042	0.0051	nil	0.012
106.	0.0020	0.119	0.0049	nil	0.029

data was: "As before, the results obtained are erratic and mostly higher than those obtained by the vacuum-fusion method for oxygen. For some reason, this Bessemer steel (No. 3) does not react properly with the iodine during the extraction of oxides. The exact reason I have been unable to ascertain, although I have given it considerable attention."

T. E. Rooney (cooperator 31) reported that improvements in the Rooney and Stapleton procedure yielded the results shown in Table 17.

TABLE 17.—*Results of Improvements in Rooney and Stapleton Procedure*

Steel	SiO <sub>2</sub> , Per Cent	FeO, Per Cent	Al <sub>2</sub> O <sub>3</sub> , Per Cent	MnO, Per Cent	Cr <sub>2</sub> O <sub>3</sub> , Per Cent	TiO <sub>2</sub> , Per Cent	Total Oxygen, Per Cent
1	0.0017	0.054	0.0062	0.055	0.0012	0.0034	0.028
2	0.025	0.0065	0.014	0.032	0.0014		0.028
3	0.017	0.021	0.0047	0.120			0.033
7	0.0010	0.446	0.013	0.027	0.0077		0.111
8	0.0029	0.030	0.037	0.0071	0.0006		0.027

Details of the improved method have not yet been published.

W. Eilender (cooperator 34) reported new determinations as follows:

Steel No.	1	2	3	4	5	6	7	8
O <sub>2</sub> , per cent	0.017	0.018	0.015	0.0019	0.0071	0.0061	0.106	0.017

These values were obtained from samples representing the full cross sections of the rods. Through a misunderstanding the values originally obtained by cooperator 34, as indicated in the main report, were obtained from samples of reduced diameter. The samples, except steel 4, were the same ones used by cooperator 18 after forging at moderate temperatures to 1 cm. diameter. Deep etching of the 1-cm. bars showed that the forging treatment had produced quite different segregation patterns from those shown in Fig. 1. Operating details of the hot extraction procedure include a furnace pressure of 0.0001 mm. or less, operating temperature of about 1700° C., and (for routine determinations) the analysis of several specimens in the same crucible. Professor Eilender's letter states: "We conclude from our work that the homogeneity of the samples was not sufficient to permit general conclusions to be drawn regarding the accuracy of the hot extraction method for the determination of oxygen. We are of the opinion that, on perfectly homogeneous material, different laboratories should obtain the same result within the usual limits of experimental error."

The Timken Steel and Tube Co., Canton, Ohio (Weston Hare, Research Dept.), should be added to the list of cooperators as No. 35. Scott's electrolytic method was used with the following modifications:

The electrolysis was carried out in a closed container in which a neutral atmosphere, free from oxygen, was maintained. At the completion of the electrolysis and without removal from the neutral atmosphere, the residue was washed with 5 per cent sodium citrate and then with copper sulphate solution to remove most of the iron and iron salts. The residue was then removed from the cell, again washed with the above reagents, then with hot 5 per cent NaOH and water and subjected to chemical analysis. Determinations of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  also were made by the hydrochloric acid method. Results obtained by both methods were as given in Table 18.

TABLE 18.—*Results Obtained by Cooperator 35*

Steel	1	2	3	4	5	6	7	8
ELECTROLYTIC METHOD								
$\text{Al}_2\text{O}_3$ , per cent.....	0.0023	0.0038	0.0030	0.0064	0.0021	0.0030	0.0027	0.031
$\text{SiO}_2$ , per cent.....	0.0017	0.013	0.0035	0.0039	0.016	0.0088	0.0015	0.0034
MnO, per cent.....	0.0020	0.0088	0.011 <sup>a</sup>	0.0044	0.0085	0.0092	0.025	0.011
FeO, per cent.....	0.015	0.0093	0.012	0.0078	0.0082	0.011	0.342	0.0097
Total O <sub>2</sub> , per cent.....	0.0057	0.012	0.0082	0.0078	0.013	0.010	0.084	0.021
HYDROCHLORIC ACID METHOD								
$\text{Al}_2\text{O}_3$ , per cent.....	0.0021	0.0043	0.0036	0.0066	0.0023	0.0031	0.0025	0.031
$\text{SiO}_2$ , per cent.....	0.0012	0.013	0.0036	0.0042	0.014	0.0095	0.0017	0.0041

<sup>a</sup> Corrected for manganese sulphide. The total manganese found in the residue was reduced by an amount equivalent to the sulphur content of the residue.

## DISCUSSION

(*John Chipman presiding*)

MEMBER.—In view of the recent spectrometric work, especially the accurate quantitative measurement of traces running up to, say, one per cent, has the method been considered for determining oxide in steel?

J. G. THOMPSON.—So far as I know, the spectroscopic method is not in use as yet for the determination of oxides in steel.

F. W. SCOTT,\* Minneapolis, Minn. (written discussion).—I should like to add a few comments in defense of wet extraction methods of oxide determination. As cooperator No. 4, I shall comment on the use of the electrolytic iodine method of oxide extraction.

1. In the summary of the paper, the authors point out that the accurate determination of very small amounts of the compounds is a separate field of analytical procedure. Any method that is limited in the size of sample, either by cost of determination, or time, or device used, limits any hope of good results. Analytical diffi-

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culty, as well as inherent nonuniform distribution of the oxides, makes good results difficult to obtain on small samples. This electrolytic method can use any size of sample, as the apparatus is very flexible in design. Solid samples are used, making possible the complete cross-section sampling. With steel, the cell may be operated many hours using the same electrolyte. A number of cells may be operated by one operator. Thus large samples may be extracted with small cost of electrolyte and labor costs. Oxide residues are large enough for accurate analysis with standard analytical methods. In this work, 100-gram samples were extracted.

2. The electrolytic extraction method is not directly comparable to the iodine-solution method. The residue, when detached from the specimen, is in a nearly neutral solution, which is low in iron salts. In high-carbon steels, or irons, the carbon clings to the specimen, and the iodine concentration is built up on the carbon, and instead of the carbon protecting the carbides, the electrolytic action aids directly in breaking up the carbides, and compounds difficult to decompose. This carbon absorbs large amounts of iron salts that must be washed out with careful, prolonged washing.

3. The results on steel sample No. 7, a rimming type, indicate that the solubility of MnO in this method is not appreciable, as nearly 100 per cent of the manganese is recovered as MnO. The FeO solubility must be low also, as nearly perfect checks are given between this method and the vacuum-fusion method. It may be concluded that the solubilities of solid particles of oxides, FeO and MnO, are low in this method. Referring to sample 1, also a rimming steel of a higher carbon content, the oxide content, based upon the calculated oxygen of the compounds, agrees very well with the vacuum-fusion results on the "rim" or the skin. Electrolytic results are the same for the zone of liquation as for the dense rim; but the vacuum fusion gives much higher results. It appears then that the oxygen in the center segregated section contains oxygen entrapped, and not as precipitated oxides. Or the oxides are so finely divided as to be not filterable.

4. In 1935 several hundred samples of pig iron were extracted and analyzed for oxides. The agreement of this method on steels with the vacuum-fusion method was accepted as demonstrating its applicability. Longer washing periods were required however. The results indicated no interference from carbides, sulphides, or phosphides.

G. R. FITTERER,\* Pittsburgh, Pa. (written discussion).—Although I have had no connection with this problem for the past few years or any of the determinations in this investigation, I have, of course, retained my interest in this subject. There are several points in this paper that should be considered generally rather than specifically.

The authors have assumed at the outset that the vacuum-fusion method accurately determines the oxygen content of steel (fourth paragraph, p. 288). If those of us who had taken the trouble to spend several years in developing new methods had thought this, we would never have started our investigations. No evidence has ever been offered that definitely convinced me that this method reduces all of the  $Al_2O_3$  and  $SiO_2$  inclusions. Tests have been made but are not convincing. Let me cite just one example of unbelievable results in this paper:

Steel No. 1 is a 0.03 per cent carbon rimming steel and contains from 0.018 per cent oxygen (or 0.082 per cent FeO) according to the vacuum-fusion method (Table 12) whereas steel No. 7, a lower carbon (0.016 per cent) rimming steel, contained about 0.106 per cent oxygen. And according to the aqueous-iodine method in the same table, sample No. 1 contains 0.006 per cent oxygen and No. 7 contains 0.095 per cent. What happened to the FeO in sample No. 1?

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I am pleased that none of the cooperators using my method attempted to determine FeO in any of the samples, because it was never recommended for that purpose. However if we consider the work of cooperator No. 20 using Scott's electrolytic method, we find that sample No. 1 contained 0.185 per cent FeO and No. 7 contained 0.480 per cent FeO. I am more inclined to believe these results than those of the vacuum-fusion method or of the aqueous-iodine method. The product of the carbon and FeO contents of steel No. 1 is 0.00555 and for steel No. 7 it is 0.0077. Both of these are of the orders of magnitude that have been calculated from a great many sources of information.

My conclusion on this work is that we should not set up a false standard, but should question the standard first and then the other methods in question.

B. M. LARSEN,\* Kearny, N. J. (written discussion).—Dr. Thompson and his associates at the Bureau of Standards have done an admirable job of reporting and summarizing a confusing group of data, and on the whole, most of their comments and conclusions seem to be fair and reasonable. We feel compelled, however, to register a strenuous objection to one of their conclusions—i.e., that “the vacuum-fusion method yields accurate results on all eight of the steels,” and their expressed belief that “the best results obtained by this method are close approximations of the true oxygen contents of each of the steels.” In the absence of more positive evidence than we now possess, this sounds a bit like an arbitrary decision by majority vote, at least sufficiently so, perhaps, to merit a “minority opinion” on the question. Among the various cooperators in this enterprise, the 15 laboratories reporting results obtained by the vacuum fusion method formed much the largest group obtaining values on these samples by a fairly well standardized procedure. Merely by the action of the laws of probability, a number of these results naturally tend to group themselves around a certain mean value, and this tendency would be equally evident whether this mean value is the true one or is merely the most probable value given by the procedure in question. It seems to us that on this basis alone we must still suspend judgment on the accuracy of these vacuum-fusion results.

The authors' argument for the more or less absolute correctness of the vacuum-fusion results seems to be based largely on their fairly close agreement with those given by the aqueous-iodine method on the killed samples in the group (Table 12). On rimmed steels 1, 3 and 7 and on the silicon-killed but high-manganese steel No. 2 it seems quite reasonable to infer that the iodine method might give low results due to partial solution of some MnO and FeO from the inclusions. However, on the remaining four killed-steel samples, the aqueous-iodine results are all higher than the “preferred values” by vacuum fusion. But even on these samples the aqueous-iodine method should give low results for total oxygen. It cannot possibly recover any oxygen actually dissolved in the metal, and is very likely to lose much of the very tiny inclusions by solution or by loss in filtrations, so that as it is perfected to eliminate contamination of the residues by carbides, basic iron salts, etc., it should then tend to give results that represent nearly all of the “microscopically visible” inclusions, but which are somewhat low with respect to the total oxygen. On this basis, it seems to the writer that Table 12 can just as well be interpreted to indicate that the vacuum-fusion results tend to be low.

From our own point of view, the fact that we have obtained much higher oxygen contents on these and many other samples by a modified hydrogen method gives us a more positive reason for suspecting the validity of this interpretation of the vacuum-fusion results. Our own results on these standard samples are those numbered 2 in Fig. 5. These values are above the “preferred ranges” given by vacuum fusion in all

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samples except 7 and 8. The hydrogen-reduction procedure used probably reduces almost none of the  $\text{Al}_2\text{O}_3$  and only a part of the  $\text{SiO}_2$  and  $\text{MnO}$  contained in ordinary steel samples, and on this basis, the total oxygen contents should be well above the No. 2 values in Fig. 5. This is especially true of sample No. 8, which contains a large amount of  $\text{Al}_2\text{O}_3$ . In my own opinion, the true total oxygen content for these samples is higher than the "selected values" by vacuum fusion by only a small percentage on sample 7, but is from 50 to 500 per cent higher in the remaining samples. In view of the possibility of such large discrepancies, it may be justifiable here to briefly review some of our own experience<sup>8</sup> with the hydrogen-reduction method and to suggest certain possible sources of error in the vacuum-fusion method.

Briefly, our procedure for the hydrogen-reduction method is to cut an average sample cross section into fine millings (0.004 in.) slowly, in air, suspend a 20-gram sample of these in a bucket of Invar in the center of a quartz bulb, remove surface oxygen by heating both bulb and sample at around 600° C. for 70 to 90 min., then heat only the bucket and sample by induction for 90 to 120 min. at around 1200° C., absorbing  $\text{H}_2\text{O}$  in a  $\text{P}_2\text{O}_5$  tube; the  $\text{CO}_2$  and  $\text{CO}$  are converted to  $\text{H}_2\text{O}$  and  $\text{CH}_4$  by a  $\text{Ni-ThO}_2$  catalyst and the resulting  $\text{H}_2\text{O}$  absorbed in a second  $\text{P}_2\text{O}_5$  tube.

With a vacuum-tight train, and with sample bucket and catalyst thoroughly reduced, we can consistently obtain blanks of 0.1 mg.  $\text{H}_2\text{O}$  or less for 2 to 3 hr. of heating, with every single condition under which the samples are run reproduced. The normal range of blank corrections is between 0 and 0.002 per cent oxygen for a 20-gram sample, and this order of magnitude is confirmed by our having obtained similar values for oxygen contents in hydrogen-reduced iron and a few steel samples.

We have been unable to find any evidence of interference by sulphur. Around 15 to 20 per cent of the nitrogen in the sample may be absorbed in the tubes as  $\text{NH}_3$ , but this corresponds to a correction of between 0.0005 and 0.002 per cent  $\text{O}_2$  for all ordinary commercial steels, including those made by the Bessemer process.

Plotting oxygen-evolution time curves for a series of special steel samples (one left without deoxidation so that  $\text{O}_2$  is present only as  $\text{FeO}$ , and the others deoxidized with  $\text{Si}$ ,  $\text{Mn}$  and  $\text{Al}$ , respectively, so that the oxygen in each could have been present only as  $\text{FeO}$  along with either  $\text{SiO}_2$ ,  $\text{MnO}$  or  $\text{Al}_2\text{O}_3$ ) gave a fairly rapid rate during the first 60 to 90 min. on all four samples, followed by a rapid falling off to a zero rate in the two samples containing either  $\text{FeO}$  only or  $\text{FeO}$  and  $\text{Al}_2\text{O}_3$ . In the remaining two samples the rate first decreased to a low value for about 30 hr. and then decreased to zero. These results indicate that dissolved and  $\text{FeO}$  oxygen are removed from such thin millings in around  $1\frac{1}{2}$  to 2 hr., but only something like 5 to 20 per cent of any oxygen present as  $\text{MnO}$  or  $\text{SiO}_2$  is recovered and that very little of the  $\text{Al}_2\text{O}_3$  (probably only extremely finely divided  $\text{Al}_2\text{O}_3$  particles) is recovered. The usual procedure on ordinary steel samples should therefore nearly always give values representing somewhat less than the total oxygen present. Oxygen-evolution time curves at one temperature for thin ribbon samples of four different thicknesses from the same steel could all be combined into one curve when corrected for thickness of material according to the theoretical diffusion formula. This result can be interpreted only by assuming that all of the substance or substances being evolved came by diffusion from within the steel and gave a single definite value for specific diffusivity, and is therefore of definite significance in establishing the validity of the method as a measure of oxygen content.

The completeness of removal of surface oxygen by our usual procedure is indicated by the following results:

1. On several samples (which either contained excess aluminum or had been treated with hydrogen at high temperatures) we obtained values varying from less than 0.001

<sup>8</sup> Reported in detail in: *Trans. A.I.M.E.* (1932) 100, 196 and (1934) 113, 61.

per cent to around 0.004 per cent  $O_2$ , after removing surface oxygen in the usual manner. This would indicate that the amount of surface oxygen left is probably negligible and at most is not more than what would be represented by a possible 0.002 to 0.003 per cent correction to the oxygen contents obtained.

2. We obtained the same surface oxygen contents from one sample of millings when separate samples were heated at 500°, 600° and 700° C. After removing surface oxygen at 500° and at 700° C. on two samples, we obtained the same values for "internal oxygen" when heating for 2 hr. at 1200° C.

In two recent groups of samples we have obtained oxygen contents by hydrogen-reduction as much as five to ten times as high as those obtained by vacuum fusion, and in both tests we had a certain amount of independent evidence that the hydrogen-reduction values were closer to the true values. Furthermore, in our general experience with the hydrogen-reduction method over about five years, it has been possible in a number of cases to correlate oxygen contents with such things as process variables or variation in certain properties of the steels, and in practically every such instance we have found a correlation that appeared reasonable and logical. For example, a series of ingots in one heat-treated with variable amounts of aluminum gave a very good correlation between grain-growth temperature and oxygen content by hydrogen reduction. In another group of steels from different heats, which were all carefully inspected for internal seams, there was a close correlation with oxygen contents by hydrogen reduction, whereas vacuum-fusion results (which were much lower in nearly all cases) showed practically no correlation. We therefore feel that, while there is still no absolutely incontrovertible proof available, there are yet definite indications of a tendency toward low values with the vacuum-fusion method even when conducted according to the most approved technique. As to possible causes of such low results, we offer the following merely as suggestions:

In general, there is good reason to believe that once having eliminated or corrected sources of "blank error" and also interference from other substances, any of these methods of analysis will always tend to give low rather than high results. In the vacuum-fusion method using the latest improved technique, blanks are satisfactorily low, and since the oxygen is present in  $CO$ ,  $CO_2$  and  $H_2O$ , which is isolated and analyzed by standard chemical methods with proper technique, the possibility of error on the high side is practically eliminated.

To avoid low values, however, the following conditions must obtain:

1. The reactions between carbon and the various solid and liquid oxides in the melt must proceed to completion at a fairly high rate of speed and the gaseous reaction products must form and be completely evolved from the melt.

2. There must be no adsorption of the evolved gases on cooler surfaces upon which vapors of iron, manganese and other metals are condensing during the heating period.

In all the work done on this method, the writer has not seen any really adequate proof that such conditions are obtained, and there are a few indications to the contrary. In conclusion, we should simply like to point out that in view of the discrepancies and uncertainties in the present available data, it would be unwise to indicate, whether by inference or otherwise, that any of the present available methods for oxygen determinations in steel give accurate results, including the vacuum-fusion and iodine extraction methods. They should all be regarded simply as research tools, the value of which must be judged solely by the usefulness of results obtained, until such time as we obtain more positive evidence regarding their relative accuracy.

J. H. SCAFF,\* New York, N. Y. (written discussion).—The authors deserve the thanks of all people interested in determining oxygen in steel for presenting these data

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to us in such good form. All of us recognize that this report covers an enormous amount of work and I think that, in spite of some discrepancies between the different methods for determining oxygen, this information will be of immediate value in standardizing methods of oxygen determination, and also that it will serve as an excellent guide for planning future work in this field.

Before I proceed with the discussion, it should be pointed out that our experience on oxygen determinations at Bell Telephone Laboratories has been primarily with highly purified iron samples. Hence we feel more qualified to discuss oxygen determinations on this type of material than on steel samples of the type covered in this cooperative program. However, there are some points brought out by our technique of analysis which deserve emphasis. The apparatus we use for these determinations differs somewhat from that usually employed. Mercury-sealed stopcocks are used throughout, and a ground glass to metal joint seals the furnace. With this arrangement we were able to reduce the nitrogen blank to negligible proportions, and this is a very desirable feature for our work. The technique used for the analysis was modified also to some extent. Since the reaction between oxides and carbon in vacuum proceeds with such violence, we adopted the procedure of melting the sample slowly at a reduced temperature and later raising the temperature to the desired value. This procedure reduces spattering to a considerable extent, but some spattering occurs, however, in spite of these precautions, and to prevent spattered metal from coming in contact with refractory oxide parts, a graphite shield was telescoped into the crucible. We found also that lower blanks could be obtained by allowing adequate clearance between the crucible and the refractory radiation shield and by supporting the crucible on beryllium oxide. Beryllium oxide proved to be extremely satisfactory as a crucible support, and we have used this material for this purpose since 1930. We are pleased to find that the experience of others that have recently used this material confirms our findings.

In our early work on oxygen determinations, we measured the evolution of gas from a sample of Armco iron in successive 15-min. intervals. Before these runs the crucible had been degassed to a point where the blank correction was negligible; namely, of the order of 0.2 c.c. of CO per hour. The results showed that the gas evolution had reached a steady state after 15 min. However, the blank correction obtained immediately following the determination was slightly larger than the empty crucible value. When additional samples were added to the crucible no further increase in blank value was noted. Consequently, we believe that blank values measured with metal in the crucible are more representative of conditions prevailing during an analysis than the empty-crucible value, and the blanks we reported to the Bureau of Standards were determined in this manner. We consider that such blanks are satisfactory if they are reproducible, and if they are small in relation to the total quantity of oxygen being determined. If these two conditions are met, it does not seem to be an important consideration if some variation in absolute magnitude is noted from time to time.

With reference to the authors' choice of acceptable ranges of oxygen for the eight samples and of the "best" value, the ranges chosen appear to be satisfactory with minor exceptions. In sample 1, for example, if the range were shifted upward 0.001 per cent, two additional analyses would have been included, with the exclusion of only one, therefore this would seem to be a desirable change, although, obviously, it is a minor change. Concerning the other results, one point warrants additional attention. Bearing in mind that our results were obtained by melting the samples slowly at a reduced temperature and subsequently increasing the temperature, it seems significant to me, that in each instance where manganese and silicon are not present together we obtained results in satisfactory agreement with the chosen best value. In samples containing both manganese and silicate we believe that our values tend to be

low and that such samples should not be analyzed by this procedure. This clearly suggests that manganese silicate inclusions have a tendency to agglomerate on remelting and that the resulting particles are not reduced completely during the time allowed for the analysis. Contrary to the authors' contention, these results show that a satisfactory recovery of oxygen is obtained using the slow melting procedure with samples containing manganese, provided only a small amount of silicate is present. Sample 3 is of this type and our determination on this material is identical with the chosen best valve. For this reason, I do not believe our low result for sample 2 is due to manganese alone but rather to the presence of manganese silicate inclusions. The magnitude of the effect is amazing; for example, if sample 2 is analyzed at 1600° C. approximately 0.02 per cent O is recovered but if it is melted slowly at 1300° C. and subsequently the crucible temperature is raised to 1600° C. only 0.004 per cent O is recovered. This indicates that agglomeration of inclusions may be an important factor in oxygen determinations by the vacuum-fusion method and perhaps that it is the principal source of error in this method. This phase of the problem surely has not received adequate attention, and more work along these lines is necessary before we can be certain of the results of the vacuum-fusion method for samples containing inclusions which show a tendency to agglomerate on remelting.

M. A. SCHEIL\* AND S. L. HOYT,\* Milwaukee, Wis. (written discussion).—We wish to compliment the authors on this paper. We are not familiar with all of the methods discussed by the authors, but our experience with wet extraction methods have included the aqueous-iodine and the electrolytic methods. The results of our limited experience with both of these methods is consistent with the interpretation of the results embodied in this paper; namely, that the results for oxygen as FeO and MnO by either method are doubtful. This we feel justifies the time and effort necessary to develop a new method for determining oxygen which gives a better picture of the distribution of oxygen among the oxides.

We do not take issue against the authors' statements concerning the fractional vacuum-fusion method, for we realize that our technique has not reached the state of refinement that eventually it will attain. However, as a metallurgical tool for gauging the quality of steel, such refinements have not interfered with our interpretation of the results to be obtained with this method. In developing this method we have correlated our interpretation of the results by observations of the visible oxides with reflected polarized light and this has enabled us to check and amplify the findings of the fractional vacuum-fusion analysis.

A. B. KINZEL,† New York, N. Y.—In the comparison of aqueous-iodine and vacuum-fusion methods, while the killed sample showed good agreement, the rimmed did not. The difference seems to approximate a constant. This indicates that there may be only a constant error, which may be found by further experimentation. The iodine method and some of the other methods give a total oxygen figure, which is divided into individual amounts for respective oxides; this is much more useful, than an undivided total value.

J. JOHNSTON,‡ Kearny, N. J.—The committee has done excellent work in its discussion of the data available to it. But I should like to supplement what Mr. Larsen said, with a plea for some further study of the hydrogen-reduction method. For it is not quite fair to conclude that this method is not satisfactorily reproducible

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‡ Director of Research, U. S. Steel Corporation.

merely because the three laboratories using it report different results. To test its reproducibility, we recently had new determinations made on these eight steels by another operator using different equipment, and all of the results except one were identical with those originally reported to the Bureau of Standards. I believe, therefore, that if a number of laboratories used this type of method, with careful attention to all pertinent details, there would be better agreement between them.

In this connection it is to be remembered that there is frequently difficulty in reconciling the analytical results reported by different laboratories with respect to constituents present in small percentages, even though those of each laboratory may be quite reproducible there. As an illustration, the proportion of sulphur reported by the several laboratories cooperating with the Bureau of Standards in the analysis of plain steel samples for sulphur, ranges from 0.046 to 0.039 per cent, the recommended value being 0.044 per cent; yet it is generally supposed, though perhaps erroneously, that sulphur in small proportions is more easily determined with accuracy than oxygen. Thus it is hardly surprising that there should be these differences in the results of oxygen determinations made at different laboratories, even by the same nominal method, therefore that we should still be unable to specify the accuracy of the data now available.

H. STYRI,\* Philadelphia, Pa.—My remarks may be a little out of order because they are not confined to oxides only. We have been interested in studying slag inclusions and consequently have approached this problem with the intention of determining both the sulphides and oxides. In many steels in which we are interested the sulphides occur to a greater extent than oxides and consequently we are just as interested in determining sulphides as the oxides. The electrolytic method has permitted us to get very good results on the sulphides but among the oxides we have been able to get only fair results on those of aluminum and silicon. We hope that improvements can be made so that we can get better determinations.

G. PHRAGMÉN,† Stockholm, Sweden (written discussion).—The large differences between the results obtained with different methods and with similar methods in different laboratories is an unmistakable evidence of the need for this cooperative work. It is to be expected that some people will be discouraged from the use of some of the methods, but also that some people will be attracted by the difficulties to be overcome. Errors have to be recognized before they can be eliminated. The large number of methods, of cooperating laboratories and of steel samples investigated has given a broad view of the present status. At the same time it has made a full consideration of every contribution almost impossible.

It is evident that the vacuum-fusion method is at present the only one giving useful results as to the total oxygen content. The spread of the results obtained by this method also is large, as is evident from Fig. 2. A continuation of the cooperative work, limited to the vacuum-fusion method would surely give valuable results. More information on the causes of error might have been obtained if all the primary results had been collected. If this material was too bulky for publication, it might anyhow have been put at the disposal of cooperators, using similar methods.

Several sources of systematic errors in the vacuum-fusion method have been discussed in the report. The risk of errors in gas analysis may have been underrated. Some possible errors have been pointed out recently.<sup>9</sup> It might be added that an Orsat or Oberhoffer apparatus is not fitted for analyzing a very small quantity of gas.

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† Metallografiska Institutet.

<sup>9</sup> G. Thanheiser: Iron and Steel Inst. meeting, Sept. 1936.

More work on this point is needed. For comparing different devices for vacuum fusion, the same gas analysis method should be used. When gas with a high nitrogen content is analyzed in an Oberhoffer apparatus, the combustion of the gas + oxygen mixture may be slow and imperfect. If some hydrogen is mixed into the oxygen (and the mixture analyzed) the combustion will be all right. This method, which was proposed by G. Ericson, has been tried in several cases, especially for high-chromium steels, and has given results consistent with those of the solution-distillation method. For steels with low nitrogen content in proportion to the oxygen content, the vacuum-fusion method generally gives lower results than the solution method.

If an error in the nitrogen content is found, the gas analysis is to be doubted. For instance, if a very low or negative nitrogen content is found for a steel, which is known to have a high or normal nitrogen content, it is more probable that the oxygen content found is too high than that some nitrogen should have been lost in the reaction vessel or in the mercury-vapor pump. If the steel contains titanium or other substances with very high affinity for nitrogen, this conclusion is not valid, of course.

For future comparative work with the vacuum-fusion method killed steels should be preferred to rimming steels; the difference between core and rim is an unnecessary source of error. The samples should be hot-worked to some dimension that can be used directly by every cooperator.

The fractional vacuum-fusion method is founded on the assumption that there is a definite reduction temperature for every oxide. The oxides, however, form compounds or solutions with each other. Even a pure oxide has no definite reduction temperature. The equilibrium of a reaction, for instance  $\text{SiO}_2 + 2\text{C} = \text{Si} + 2\text{CO}$ , is given by an equation

$$\frac{\{\text{Si}\}[\text{CO}]^2}{\{\text{SiO}_2\}[\text{C}]^2} = f(T)$$

if  $\{\text{Si}\}$ , etc., be the activities with the pure substance as standard, and  $[\text{CO}]$  the pressure of CO. Thus the equilibrium temperature depends on the pressure in the reaction vessel and on the silicon content of the molten iron. The apparent reduction temperature is, of course, higher than the equilibrium temperature, and the difference is not fixed.

The velocity of the reactions between the molten steel and the slag inclusions is great.<sup>10</sup> Thus, the content of  $\text{FeO}$ ,  $\text{MnO}$ ,  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  in slag inclusions of ordinary magnitude will be approximately determined by the composition of the steel. The reduction temperature observed may be influenced by the composition of the steel in the same degree as by the composition of the inclusions. Of course, when the fractional method is used, only one sample is to be melted in the graphite crucible. If, for instance, some pure iron is melted first in the crucible, the reduction temperatures will be lower.

In some cases the residual methods may give more information than the vacuum-fusion method. If the oxide inclusions in steel, melted under a basic slag, contain calcium or magnesium it is very probable that they originate from the slag.

ISTITUTO SCIENTIFICO TECNICO ERNESTO BREDA,\* Milan, Italy (written discussion).—We communicated to the National Bureau of Standards with our reports of May 23 and Nov. 29, 1935, the results we obtained in the dosage of total oxygen by the vacuum fusion method in a graphite spiral furnace, by using the equipment described by Meyer and Castro<sup>11</sup> and in the dosage of the inclusions of oxides with the iodine

<sup>10</sup> R. Perrin: *Rev. de Mét.* (1933) 1, 71.

<sup>11</sup> O. Meyer and R. Castro: *Arch. Eisenhüttenwesen* (1932) 6, 189.

method of Eggertz modified by Cunningham and Price<sup>12</sup> and we adopted this method in pursuance of the request of the National Bureau of Standards. The determinations took place on eight rods of steel supplied by the National Bureau of Standards, whose instructions were carried out to the letter for withdrawal of the parts of the sample to be assayed.

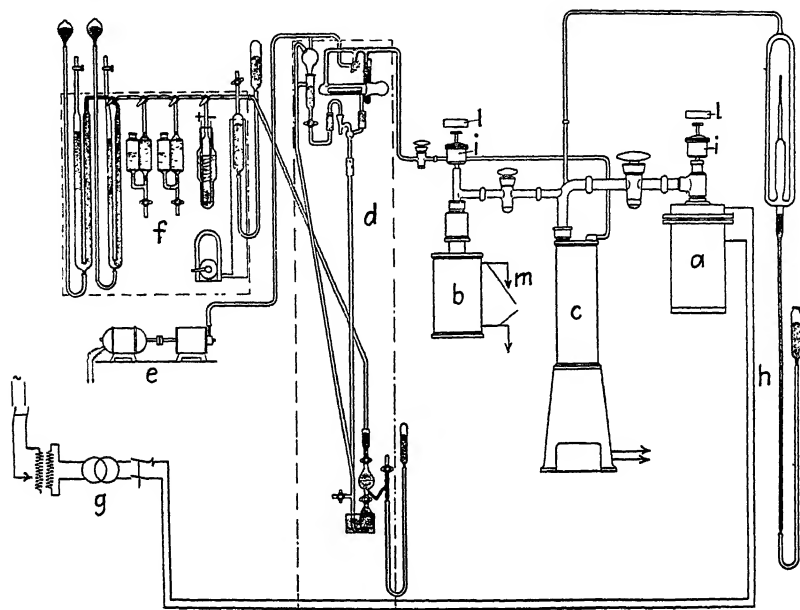


FIG. 10.—SCHEME OF APPARATUS FOR TOTAL OXYGEN DETERMINATION BY VACUUM-FUSION METHOD, USING EITHER GRAPHITE SPIRAL FURNACE OR HIGH-FREQUENCY INDUCTION FURNACE.

- a, graphite spiral furnace.
- b, high-frequency induction furnace.
- c, mercury-diffusion pump.
- d, jet mercury pump.
- e, rotary oil pump.
- f, gas analyzer.
- g, electrical equipment for the graphite spiral furnace.
- h, vacuum gauge (MacLeod).
- i, drum apparatus for introduction of samples into furnace.
- l, mirror to observe furnace inside and to measure temperature.
- m, leads to high-frequency converter set.

Some considerations are given here on the final results of the investigations that are the subject matter of the paper under discussion. These considerations regard the determination of total oxygen and oxides with the methods we adopted.

#### *Determination of Inclusions of Oxides with Iodine Method*

Our results, together with those of four collaborators, have been used to establish the "limits of acceptability" of the values obtained with the various iodine methods. When giving our results, however, we pointed out the trouble resulting, because, when operating as Cunningham and Price prescribe on a sample of 5 grams, the quantity of the various oxides contained in the residues was so small as to equalize in many

<sup>12</sup> T. R. Cunningham and R. J. Price: *Ind. Eng. Chem. Anal. Ed.* (1933) **5**, 27.

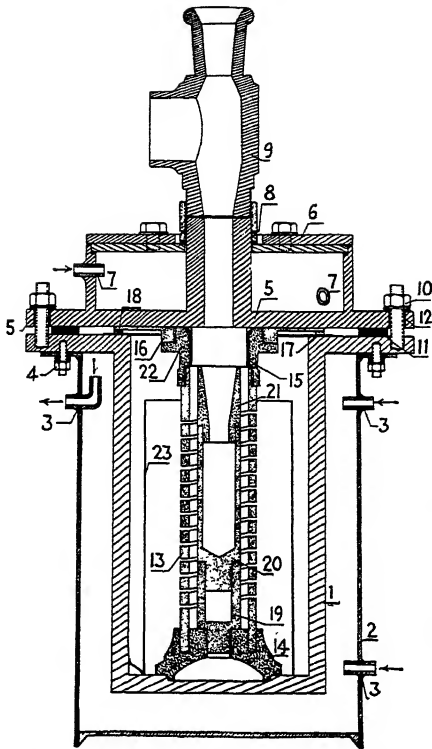


FIG. 11.—LONGITUDINAL SECTION OF GRAPHITE SPIRAL FURNACE.

- 1, main body of furnace, low-carbon steel, one piece.
- 2, water jacket, low-carbon steel, welded.
- 3, intakes for furnace-cooling water, steel.
- 4, bolts for outside covering, steel.
- 5, furnace cover, steel, one piece.
- 6, bracket.
- 7, intakes for cover-cooling water, steel.
- 8, bolt to close cover, steel.
- 9, connection to diffusion pump and apparatus for introduction of samples, steel.
- 10, bolts to close furnace, steel.
- 11, gasket, hard rubber.
- 12, insulating rings.
- 13, spiral resistance, graphite.
- 14, support of the spiral, graphite.
- 15, shield for the spiral, graphite.
- 16, contact plate, copper.
- 17, insulating ring, mica.
- 18, metallic ring, steel.
- 19, crucible support, graphite.
- 20, crucible, graphite.
- 21, crucible funnel, graphite.
- 22, spiral top, graphite.
- 23, shield, molybdenum.

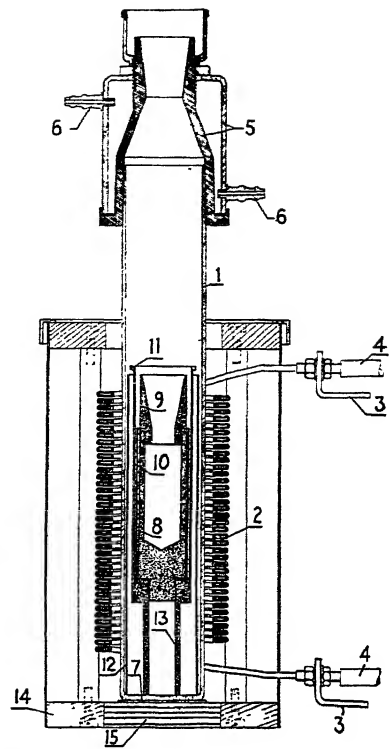


FIG. 12.—LONGITUDINAL SECTION OF HIGH-FREQUENCY INDUCTION FURNACE.

- 1, silica tube.
- 2, copper spiral.
- 3, terminal connections.
- 4, intakes for spiral-cooling water.
- 5, steel hood.
- 6, intakes for hood-cooling water.
- 7, porcelain plate.
- 8, graphite crucible.
- 9, graphite funnel.
- 10, molybdenum-sheet cylinder.
- 11, graphite shield.
- 12, molybdenum shield.
- 13, graphite support.
- 14, frame.
- 15, asbestos.



cases the value of the blank test when their dosage was proceeded with. With  $\text{FeO}$  and  $\text{Al}_2\text{O}_3$ , this trouble was made worse by the fact that their dosage took place on an aliquot part of the solution of the oxides corresponding to 2 grams of the sample. From the foregoing it was clear that the unavoidable experimental errors would influence the final results to a rather considerable extent. We were then of the opinion, as we are now, that to obtain reproducible results with the iodine method it is necessary

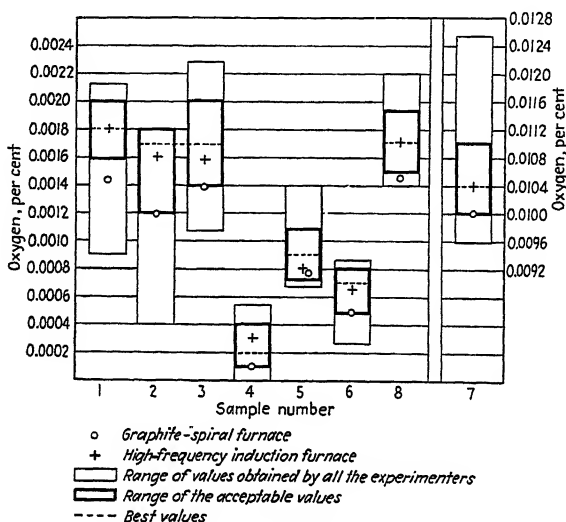


FIG. 13.— COMPARISON BETWEEN VALUES OBTAINED WITH OUR APPARATUS AND ACCEPTABLE AND BEST VALUES ESTABLISHED BY THE COMMITTEE.

to work with larger quantities of samples than those laid down by Cunningham and Price. This end can perhaps be gained by carrying out the dosage of the various oxides with microanalytical methods properly chosen and studied pursuant to what some experimenters have done recently, who took the problem in hand. Examination of the results obtained by various cooperators has led us to come to the conclusion that for the purpose of having reliable values with the iodine method it is necessary to define its field of application as well as possible, because it is clear that the resistance of the inclusions to the solvent action of the iodine depends on their nature and on their composition.

#### *Determination of Total Oxygen by the Vacuum-fusion Method*

When giving the results of determination of the total oxygen, obtained with the hot extraction method in a graphite spiral furnace, we pointed out our suspicion, which has now been confirmed by the paper under discussion, that they were slightly inferior to the real oxygen contents. We wish to mention, however, that the said results enter into those declared to be "acceptable" in regard to samples 2, 3, 4, 5, 6 and 7, and they are only slightly lower for samples 1 and 8. To explain the failures noted, we thought that they might depend, at least partly, (1) on the fact that a certain quantity of material did not undergo the reaction due to the spattering of metal taking place during the melting of the samples and (2) on the carbon oxide absorbed by the cold graphite parts, and perhaps also on the reactions between gas, graphite ashes and metallic sublimates.

In the first case the trouble could have been lessened considerably if the steel samples placed at our disposal had a smaller diameter so as to allow small cylinders including the complete cross section of each rod to be put in the furnace but it was absolutely impossible for us to do this because of the characteristics of our equipment, which compelled us to cut the various disks (weighing 7 to 8 grams) in four pieces, which, on account of their limited size, melted almost at once, causing a tumultuous development of gas. In regard to the second supposition, with our paper of Nov. 29, 1935, we communicated to the National Bureau of Standards the results of some determinations of total oxygen carried out after having suitably shortened and widened the canalization for the evacuation of our equipment. The aim of these experiments was to see if, by helping quick extraction of the gases freed by the melted metal, it was possible to reduce the oxygen losses to a minimum, which were due to reactions between the gases, the cold parts and the graphite ashes and the metallic sublimates. The results obtained, however, were practically the same as those previously communicated, and they proved that the changes in our equipment had not led to any improvement. It was then decided to push the investigations deeper by repeating the determinations with a high-frequency induction furnace, which had been got ready in the meantime, leaving the rest of the equipment unchanged.

Our equipment is schematically illustrated in Fig. 10. The graphite spiral furnace used for the previous experiments is shown in section by Fig. 11 and it is substantially different from that which was described by Meyer and Castro on account of the fact that the graphite spiral, instead of being supported by a metal cage, rests with its support (14) on the bottom of the furnace and cleaves with the upper part (22), by means of the wings of the copper plate (16) clasped between the flange of the cover and the furnace itself. In this way the danger is done away with, which is caused by the presence in the inside of the furnace of metallic parts and insulating refractory masses. The graphite spiral is put in and taken out with the help of a metallic rod, which is made rigid by fixing it at the ends by means of threads. The upper part of the spiral, which is more exposed to spattering of metal and more apt to become covered with sublimates, is protected by a graphite shield (15) that can easily be changed when necessary. The high-frequency induction furnace with which we repeated the determinations of the total oxygen is

TABLE 16.—*Details of Vacuum-fusion Procedures*

Furnace	Operating Temperature, Deg. C.	Crucible Support	Thermal Insulator	Blank Correction		Sample Weight, Grams	Number of Samples in Crucible	Surface of Melt	Average Time of Run, Min.	Gas Analysis
				CO per Hr., c.c.	Oxygen, Per Cent					
Graphite spiral. . . . .	1750	Graphite	Molybdenum	0.16-0.20	<0.001	7-8	8	Funnel top	15	Atmospheric pressure Oberhofer
High-frequency induction	1680	Graphite	Molybdenum and graphite	0.16-0.20	<0.001	7-8	8	Funnel top	15	

outlined in Fig. 12. It differs from Hessenbruch's original furnace in that: (a) the hood is made of stainless steel instead of glass; (b) two screens are used, namely, one of a molybdenum sheet (12) and the other of graphite (11) and they are both cut along a generatrix to avoid having them heated by induction currents, the task of these screens being to avoid excessive heating of the quartz tube due to radiation, and to allow quick heating of the crucible (8) so as to reduce to a minimum the time required for outgassing; and (c) a molybdenum sheet screen (10) is placed between the graphite shield and the crucible, to increase the furnace's performance.

Details of the vacuum extraction processes used for the two furnaces are given in Table 16. The results obtained are shown in Table 17 and Fig. 13. The position in which they are in regard to the "limits of acceptability" and to the "best values" established by Messrs. Thompson, Vacher and Bright is shown in Fig. 13. From an examination of these results it will be seen that those obtained with the induction furnace are somewhat higher than those obtained with the graphite spiral furnace,

TABLE 17.—*Oxygen Percentages Obtained by Vacuum-fusion Method with High-frequency Induction Furnace*

Steel ¼ <sub>7</sub>		Steel ¾ <sub>4</sub>		Steel ¾ <sub>3</sub>		Steel ¾ <sub>4</sub>		Steel ¾ <sub>9</sub>		Steel ¾ <sub>0</sub>		Steel ¾ <sub>4</sub>		Steel ¾ <sub>3</sub>	
1	0.0185	1	0.0150	1	0.0152	1	0.0027	1	0.0079	1	0.0065	1	0.1030	1	0.0166
2	0.0186	2	0.0161	2	0.0165	2	0.0038	2	0.0073	2	0.0059	2	0.1040	2	0.0160
3	0.0186	3	0.0171	3	0.0150	3	0.0024	3	0.0086	3	0.0072	3	0.1037	3	0.0172
4	0.0169	4	0.0164	4	0.0152	4	0.0026	4	0.0088	4	0.0061	4	0.1052	4	0.0176
														5	0.0173
Average.....	0.0181		0.0161		0.0155		0.0029		0.0082		0.0064		0.1040		0.0169

and that they are practically the same as the "best values." The improvement of the results might depend on the convective movements of the melted metal mass, which favor carburization and therefore reduction of the oxides, and also on the lower temperature of the furnace, which keeps down the extent of the metal splashes and hence reduces the causes of mistakes. It is not to be overlooked, however, that this improvement may depend, at least partly, on the absence of cold graphite parts in the furnace, which could produce the troubles as per point *b* just above.

The results of our experiments, therefore, lead us to consider that with the graphite spiral furnace of the type we used, a degree of exactness can be obtained for the total oxygen that will satisfy normal requirements. However, at the present time the induction furnace should be preferred if results of notable exactness are to be obtained.

T. E. ROONEY,\* Teddington, England (written discussion).—Regarding the *Alcoholic Iodine Method*, we would say:

*Al<sub>2</sub>O<sub>3</sub>*.—The statement on pages 269 and 270 with regard to the values obtained by the Rooney and Stapleton procedure for alumina needs some modification. On steel No. 2, cooperators 22 and 31 report high values and a subsequent check by 31 yields 0.0136 per cent. On steel No. 3 cooperator 27 reports a high value and a subsequent check by 31 yields 0.0047 per cent. The values for steel No. 7 are also high, a check determination by 31 yielding 0.0129 per cent.

*SiO<sub>2</sub>*.—With regard to the high values reported by cooperators 22 and 31 on steels 2 and 3, check values by 31 yield 0.025 and 0.0167 per cent, respectively. It is prob-

\* Metallurgy Department, National Physical Laboratory.

able that the selected values based on the aqueous-iodine method are low because of the solubility of the silicates as noted at the top of page 274.

*MnO.*—The high values reported by the alcoholic iodine method may be due to some extent to the presence of some MnS in the residue, especially with steel No. 3. A check determination by 31 on No. 3 yielded 0.120 per cent. The low value reported by cooperator 27 is due to the fact that sulphur was estimated in the residue and a corresponding deduction made from the MnO value. The value was probably over-corrected, as the sulphur may not be wholly present as MnS.

The values for MnO by the alcoholic iodine method agree with those by the fractional vacuum-fusion method for steels 1, 2, 5, 6 and 8 but for No. 7 no MnO value is recorded by the vacuum-fusion method.

The selected value for MnO may be too low, as it is questionable whether this constituent is quantitatively recovered by the aqueous-iodine method (see p. 272, paragraph 2; bottom of p. 286, and p. 274, paragraph 2).

*FeO.*—The presence of sulphur and phosphorus in the steel may have an effect on the amount of FeO recovered as noted for MnO. Recent work indicates that a long churning period or maintaining the reaction temperature at about 60° C. yields lower values. It is highly probable that even when the inclusions consist mainly of silica and alumina, a small amount of FeO will be combined with these constituents. One can agree with the statement on page 269 that inaccurate chemical analysis of the insoluble residue is responsible in part for some of the variations in the results.

The formation of an Oxygen Panel of the Committee on the Heterogeneity of Steel Ingots of the Iron and Steel Institute has enabled cooperators 22, 27 and 31 to meet and exchange information and methods. This procedure has tended to eliminate variations in the values reported by the three laboratories and consequently some of the extreme values in the Bureau of Standards report may be disregarded.

It is interesting to compare results of the alcoholic iodine method with those of the fractional vacuum-fusion method. The values for MnO have been commented on already. For silica there is agreement on steels 1, 4 and 5 and in other cases the values lie within the selected range. For steels 7 and 8, values are high by the fractional fusion method but on the other hand the alumina values are low. The values for alumina on steels 3, 4, 5 and 6 are in agreement.

Low values are reported for FeO (in some cases nil) by the fusion method. This may mean that the FeO fraction when small in amount is difficult to separate from the MnO fraction. In any case, the volume of the gas fraction must be very small from 11 grams of steel.

The FeO values by the alcoholic iodine method are consistently high but, as before noted, improvements that have been made on the method should result in somewhat lower values.

*Authors' Comments.*—It is agreed that the estimation of the very small amounts of constituents needs a special technique and a skilled analyst and even then it is difficult to realize the degree of accuracy desirable in the analysis of the smaller of the residues from the iodine method. The work of the Oxygen Panel has helped to standardize the procedure for the alcoholic iodine method and has resulted in much better agreement in the determinations by the three laboratories using the method. One cannot agree that the accuracy of the aqueous-iodine method has been established as there is very wide variation between the results of the various cooperators.

*Hydrogen-reduction Method.*—The statement on page 277 that this method is generally assumed to recover only the oxygen present as FeO or MnO may need some modification. It has been shown that silica in contact with iron can be reduced by hydrogen at about 1200° C. Also, it may be possible to reduce alumina judging from the appreciable blank obtained when using an alumina boat in contact with iron millings.

The surprising feature of the results recorded is that cooperator 5, using a tin-antimony alloy and a temperature of 1080° C., obtains consistently high results. In the writer's experience this method usually gives slightly lower values than direct reduction at 1200° C. Also, the alloy in dissolving the steel tends to separate silica, etc., which floats on the surface and is not reduced.

The use of high-frequency induction heating is interesting and was advocated by the writer some years ago. It should be a step in the right direction, but the results recorded with the exception of steels 7 and 8 are on the high side. It is difficult to account for the low result on No. 7. It may be due to the preheating of the sample. It is also difficult to account for the variation in the values on steels 2, 4, 5 and 8 by cooperators 17 and 32, who appear to be using very similar methods.

H. A. SLOMAN,\* Teddington, England (written discussion).—The report on the vacuum-fusion method is of considerable interest. However, the method adopted in obtaining the accepted ranges and best values is arbitrary, particularly as to the sizes of the boxes. Why, for instance, should the ranges for steels 1, 2, 3 and 8, all of which contain approximately the same total oxygen, be of different sizes? For steels 1 and 8, the range is 0.004 per cent whereas for 2 and 3 it is 0.006 per cent.

The writer, cooperator 31, is in agreement with the general recommendations on p. 262, except for the sentence that says: "Spattering of the melting sample or of the molten bath should be prevented, but a satisfactory, reliable and convenient means of accomplishing this end has not yet been developed." The use by several cooperators, including the writer, of a graphite ball or valve answers all these requirements. Duplicate analyses of steels of many types carried out in the writer's apparatus give results that are in good agreement, and show this type of lid to be entirely reliable and convenient.

The writer is in agreement with the reviewing committee as regards his own results. The method of sampling would undoubtedly tend towards high values for rimming steels, and particularly for No. 7.

It cannot be agreed that the vacuum-fusion method is in agreement with the aqueous-iodine method. In no test do the selected values for the latter method fall within the boxes for the former, therefore the statements in the two top paragraphs on page 275 are without adequate foundation.

The results of cooperator 24, using a fractional vacuum-fusion method, are interesting, but surely a sample weighing only 11 grams leads to serious inaccuracies, particularly when the total oxygen is low, and this has to be subdivided into four or more fractions.

F. KÖRBER,† Düsseldorf, Germany (written discussion).—In consideration of the possible sources of error in the determination of oxygen by the hot extraction method, the influence of condensed manganese vapor must be given especial consideration.

Researches on the influence of manganese, carried out at the Kaiser-Wilhelm-Institut für Eisenforschung at Düsseldorf,<sup>13</sup> have shown that details of operation, for example, the manner of cooling, are important as well as the amount of manganese present.

To illustrate the effect of the conditions of deposition and cooling of the manganese deposit on the results obtained for oxygen in the cooperative samples, steel 2 (1.15 per cent Mn) was investigated under different conditions of cooling. The apparatus

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† Kaiser-Wilhelm-Institut für Eisenforschung.

<sup>13</sup> G. Thanheiser: *Stahl u. Eisen* (1936) 56, 1125.

described by Thanheiser and Brauns<sup>14</sup> was used and the only variation in procedure was that in one instance the furnace tube was cooled by means of a water jacket; in the other, a copper cooling coil was used. In a third experiment, the manganese was condensed in a graphite bell, which was then lowered so that the condensed manganese could be heated, as described by Thanheiser (ref. 13). Before each determination approximately 80 grams of manganese-free iron was melted in the crucible. The operating temperature was 1550° C.; the use of a four-stage diffusion pump and large-diameter glass tubing permitted rapid removal of the evolved gases. The results are shown in Table 18.

TABLE 18.—*Influence of Cooling on Results of Oxygen Determinations by Hot Extraction Method*

Manner of Cooling	Per Cent Oxygen
Intensive water-cooling (water jacket).....	0.007 , 0.008
Copper cooling coil.....	0.018 , 0.017
Copper cooling coil plus condensation of manganese in graphite bell.	0.018 , 0.018

It is evident that the manner of cooling, other conditions being equal, appreciably influences the effect of condensed manganese in the determination of oxygen. When the gases are rapidly extracted and the details of procedure are carefully specified, correct results will be obtained in each apparatus and good reproducibility in the determination of oxygen will be obtained in different laboratories.

The cooperative analyses have again shown how valuable is an exactly operated method for the determination of total oxygen. The reliability of individual residue methods can be established only by means of a reliable determination of total oxygen.

P. KLINGER, in collaboration with H. FÜCKE AND W. KOCH,\* Essen, Germany (written discussion).—Something unusual has been accomplished in this investigation. It is the first time in the controversial history of oxygen determination that a cooperative effort of such an extent has been carried out. The participation of 34 authoritative laboratories in eight different countries, where the production of iron and steel is highly developed, makes the investigation international in character and thereby particularly valuable. We therefore express our appreciative recognition to the sponsors of this enlightening undertaking, and especially to the Bureau of Standards.

General inspection shows a considerable spread in the results and also shows that the different methods are by no means equivalent. In a general comparison of the results it is impossible to eliminate the personal point of view. The reasoning in connection with the discarding of scattered values is clear and good; we agree with the considerations and with most of the conclusions. However, the following comments are offered:

In our practice we have adopted the vacuum-fusion method for the determination of total oxygen because of the reproducibility of results obtainable by this method. The operating temperature of 1900° C., ascribed to us in the report, is the maximum used, the average reduction temperature is about 1800° C. Spattering of gas-rich specimens during melting is prevented by lowering the temperature before the sample

<sup>14</sup> Thanheiser and Brauns: *Mitt. K-W-I Eisenforschung*, Düsseldorf (1935) 17, 207.

is introduced. To eliminate as far as possible the influence of manganese, we first place low-manganese iron in a new crucible before adding the high-manganese sample. The results of the cooperative study show that complete reduction is obtained in a shorter time in the high-frequency furnaces (15 min.) than in the graphite spiral furnaces (20 to 30 min.). This is due to the vigorous stirring of the high-frequency melt.

In our opinion the fractional vacuum-fusion method is not suitable for a quantitative determination of individual oxides because a steel contains not only pure oxides, with fairly sharply defined reduction ranges, but also combinations of oxides. Furthermore, at a given temperature secondary reactions occur between constituents of the steel and thereby render uncertain the data obtained for the origin of the recovered gases.

In the hydrogen-reduction method it is remarkable that the results, with few exceptions, are higher than the values for total oxygen obtained by vacuum fusion. Only in steel 7, with only 0.02 per cent Mn, are the results of both procedures in practical agreement.

In regard to the chlorine method, it should be noted that the chlorinating temperature of 500° C. (cooperator 17) is decidedly too high for the determination of FeO and MnO, since at temperatures above 400° C. the oxide inclusions of iron and manganese are decomposed.<sup>15</sup> The values obtained by cooperator 17 for iron and oxygen contents are undoubtedly low. The residue obtained by us through chlorination at 350° C. contained no metallic particles, as was suggested in the report.

In regard to the iodine method, we are astonished that the value for total oxygen derived from the selected values in steels 1 to 3 is only about 50 per cent of the vacuum-fusion value for total oxygen, because it is probable that in steels 2 and 3 the vacuum-fusion results are somewhat low on account of the high manganese contents. Since decomposition of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> in the iodine solution is improbable, it follows that FeO and MnO cannot be entirely stable in the iodine solution. Moreover, it is doubtful whether hydrolysis can be completely avoided even in alcoholic solutions.

In evaluating the results of all of the residue methods, the first consideration is the difficulty involved in the analysis of only a few milligrams of residue material. We agree entirely with the emphasis that the reviewing committee has placed on this point.

In forwarding our results in June 1935, we remarked that exhaustive investigations have shown that microchemical methods are essential for the separation and analysis of the residues isolated by the various procedures. Since then we have studied this matter and have applied photometric-micro methods, by which specimens of less than 0.1 mg. may be quantitatively determined, so that these methods find application in the analysis of residues. The determination is made by measuring the extinction in a "Polaphot" polarization photometer made by Carl Zeiss, in Jena, and interpreting the results by means of a calibrated concentration-extinction graph. Full details of the procedure will soon be published in *Archiv Eisenhüttenwesen* or *Tech. Mitt. Krupp*.

In our report of June 1935, we mentioned that in the field of electrolytic methods we have followed the procedure of Benedicks. In the past year we have studied the matter further and have concluded that SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, FeO, MnO, FeS and MnS may be thereby determined. The results are reproducible in repeated determinations on the same material. The method will be described in detail in the near future (*Archiv Eisenhüttenwesen* or *Tech. Mitt. Krupp*) and is briefly as follows:

Consideration of the discharge potentials of oxygen and hydrogen led R. Treje and C. Benedicks to adopt the electrolyte consisting of a 5 to 10 per cent solution of copper

<sup>15</sup> See *Stahl u. Eisen*, (1929) 49, 1263.

bromide at the cathode and a 0.1 N solution of potassium bromide, containing 15 per cent of sodium citrate, at the anode. Sometimes KI solution was added to the anolyte. We did not use collodion thimbles; the anolyte was continuously replaced with fresh solution and an atmosphere of nitrogen was maintained, whereby the pH of the solution was kept constant at  $7 \pm 0.2$ . The theoretical amount of iron goes into solution. There are no secondary reactions at the anode.

The residue from the electrolysis was divided into two parts, without drying. MnO was extracted from one part, using glycochol solution, permitting the determination of FeS and MnS in the residue. The other portion was treated with copper bromide solution, whereby all constituents except FeO ( $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ ) were decomposed. The FeO was dissolved from the residue with acid. In the purified residues from both portions  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  were determined as well as the FeO and MnO combined therewith.

All determinations were made by the microchemical method previously referred to, in which amounts of a few millionths of a gram may be accurately determined.

TABLE 19.—*Electrolytic Determinations*

Steel No.	Percentages						Oxygen	
	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	FeO	MnO	FeS	MnS	Combined with Fe and Mn	Total
4	0.010	0.0022	0.031	0.009	0.032	0.022	0.009	0.015
	0.011	0.0017	"	0.013	0.038	0.021	0.009	0.016
5	0.019	0.0003	0.038	0.008	0.056	0.031	0.010	0.020
	"	0.0004	0.032	0.007	0.033	0.028	0.009	0.019
7	0.007	0.0005	0.31	0.0021	0.019	0.022	0.070	0.074
	0.006	0.0008	0.35	0.0026	0.026	0.020	0.079	0.083

\* Determinations were spoiled. The companion determination was used for computing the total oxygen.

We have used this electrolytic method for additional determinations on steels 4, 5 and 7, with the results shown in Table 19. Comparing these results with those published in the report, it is evident that there is good agreement between the hydrogen-reduction results of cooperator 2 and our results for steels 4 and 7, which are low in carbon and  $\text{SiO}_2$ . For steel 5, with its higher carbon and  $\text{SiO}_2$  contents, the results of cooperator 2 are higher than ours. Our experience has been that carbon at  $1100^\circ \text{C}$ . in an atmosphere of hydrogen exerts a reducing action on  $\text{SiO}_2$ . Furthermore, there is good agreement of our results for  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and FeO for steels 4 and 5, with corresponding results obtained by the chlorine method. The computed value for total oxygen for steel 7 is in satisfactory agreement with the determinations by the vacuum-fusion and hydrogen-reduction methods. It is interesting to us that our calculated values for the oxygen contents of steels 4, 5 and 7 increase with decreasing manganese contents, as is also true for the results of the vacuum-fusion procedure, a phenomenon that G. Thanheiser<sup>16</sup> has also observed in the presence of higher manganese contents.

<sup>16</sup> G. Thanheiser: *Stahl und Eisen* (1936) 56, 1128.



We recommend that the cooperative effort be continued in some form. The work should be extended with accurately specified procedures, identical apparatus and fully described analytical methods.

G. F. STAMMLER, Summit, N. J. (written discussion).—This paper is most opportune, as it has given a summary of the results obtained by the various methods, and permits an unbiased opinion on the merits of the different procedures. The writer is most familiar with the iodine method and is still of the opinion that this procedure gives most information. It tells how the oxygen (present as metallic oxides) is combined, and this is not done satisfactorily by the other methods.

The determinations of silica and alumina depend chiefly on the care of the analyst: and when any of the weak solvents are used, the results show consistency. When stronger acids are used, they offer the advantage of permitting larger charges. The nitric and hydrochloric acid methods have the disadvantage that the acids and alkaline treatment of the insoluble residue have a solvent action, which is dependent upon the composition of the inclusions; i.e., a high-silica inclusion is active up to a lesser degree than a low-silica inclusion.

In the iron oxide determinations, the fractional vacuum-fusion results appear to be low, and part of the iron oxide has been counted with manganese oxide. The operators of the electrolytic method state that sulphides are also reported in the results published, so they do not give much information on the oxide content.

The figures for manganese oxide offer the greatest proportionate range for most of the wet methods. Some of these are due to inaccurate work on the part of the analysts, especially in steel No. 7 (for both the iodine and mercuric chloride method) when more manganese oxide was reported than the total manganese content of the steel. For steel No. 3, the high MnO figures may be due to undissolved manganese sulphide. It has been the writer's experience that manganese sulphide is not dissolved in the iodine solution as readily as the metal or carbide, and a high-sulphur steel must be acted upon by the solvent for a longer period to be certain that the manganese sulphide is entirely dissolved.

The results for MnO by the fractional vacuum-fusion method indicate that the gases contained in the steel are drawn off at this point, as shown by the high MnO figures for steels 1, 2 and 3.

The electrolytic methods show generally high results for the MnO and claim they are due to manganese sulphide. This might account for the higher amounts for steel No. 3, but is not a satisfactory explanation for the high figures reported for steel No. 2 when compared with steels 6 or 8. The two latter steels contain slightly higher sulphur than No. 2 steel, but most of the operators of this method report higher MnO plus MnS for No. 2 than for the other two steels (cooperator No. 20 being the exception). In addition to the oxides and sulphides, the writer believes that some manganese carbide is also included.

In the list of results in the "accepted range" for the iodine method, it is generally noticeable that the manganese oxide follows the silica, except for steel No. 7. In the remaining seven steels, the manganese oxide is present as manganese silicate, but in steel No. 7 we have a great amount of iron oxide and the manganese oxide is soluble in iron oxide. The iodine method thus gives information that the so-called "residual manganese" in a heat may be entirely manganese oxide; and when such is the condition, the metal is also saturated with iron oxide.

In the iodine method we do not determine the oxygen combined as a gas and the presence of gas in rimming steels is a well-known fact. Split ingots show a great number of blowholes and the gas contained in these cavities has been found to be chiefly carbon monoxide. In steel No. 2 we also have considerable dissolved or entrapped carbon monoxide gas, which may be due to the fact that hot metal was

added to the ladle, and because of the silicon and high manganese content of the steel, we had more rapid solidification of the ingot. These four steels (1, 2, 3 and 7) contain gases, and this fact is further verified, not only by the results of the iodine and vacuum-fusion methods but also by the etch tests shown in Fig. 1. The etch tests show that these steels have porous centers and this porosity is due to gases, chiefly CO.

In the summary of the data on the accuracy of the vacuum-fusion and iodine methods, it has been assumed that the iodine results were correct for steels 4, 5, 6 and 8, but low for the remaining four steels. If we consider the results from the standpoint of "total oxygen in the steels," the vacuum-fusion results are correct for these four steels (1, 2, 3 and 7) and the iodine figures are low. But if the subject is considered from the standpoint of how the results were reported (i.e., the oxides of silicon, aluminum, iron and manganese), the percentages reported by the iodine method are also correct.

J. G. THOMPSON, H. C. VACHER AND H. A. BRIGHT (written discussion).—The discussions are a valuable contribution to this cooperative attempt to define more precisely the reproducibility and accuracy of the methods for the determination of oxygen. The suggestions should be used as a guide for correcting current procedures and for future research work.

Inasmuch as this is a report on a cooperative project giving a collection of values from widely different sources, we feel that many of the questions brought out in the discussions are a matter of opinion and for that reason an individual and detailed answer is not necessary. However, we should like to reply to some of the questions raised.

It was suggested that the spread of the values might be largely caused by segregation. This does not seem probable. Precautions were taken to prevent segregation in the rods and the rods were sampled and analyzed before the analytical samples were distributed. The spread of the values obtained from these samples in the preliminary examination was considerably less than the spread of the values subsequently submitted by the cooperators. Our opinion was and still is that the results obtained by different cooperators are, in general, within the reproducibility of the various methods. However, the reproducibility of the methods as used by the cooperators is not good. The spread of values is large and the position of a cooperator's value within the spread is rarely the same for all the steels. These facts indicate strongly that the value obtained by a method is influenced greatly by small variations in procedure. We are heartily in agreement with the suggestion that future work should include investigations of the effect of small variations in procedure, and to this end we made recommendations for the vacuum-fusion method. Considerable improvement in the reproducibility of the residue methods could be made by perfecting the procedure as has been done recently for the electrolytic iodine method.

The conclusions that "the vacuum-fusion method yields accurate results for all eight of the steels" and "that the best results obtained by this method are close approximation of the true oxygen contents of each of the steels," appears to some as being unjustified. These conclusions represent the authors' opinion, based on the cooperators' reports and on our experience. The agreement of results obtained by two independent methods was the criterion used for these conclusions, assuming that agreement in results obtained by two independent methods indicates that both methods yield accurate results. In our opinion the "best" values of the aqueous-iodine method are close approximations of the oxygen content for steels 4, 5, 6 and 8 and the "best" values for the vacuum-fusion method are in substantial agreement with these values. Our experience indicates that the vacuum-fusion method would tend to give low values for these types of steels but should give correct values for steels 1, 2,

3 and 7. Therefore we conclude that the vacuum-fusion method gives a close approximation of the true oxygen content for each of the eight steels.

We are in agreement with the opinion that there is as yet no "incontrovertible proof" of the correctness of any method and that further research is necessary. In this respect we believe that the accuracy of any method must be determined by an investigation of several methods applied to a carefully selected series of steels, whose compositions should be such that at least one method would in all probability give correct values. An example of such a series would be low-carbon steels completely killed with Al and containing increasing amounts of Mn. We believe, however, that further attention must be devoted to the details of procedure before the accuracy of the various methods can be satisfactorily determined.

# Fractional Vacuum-fusion Analysis for Determination of Oxygen in Steel

By S. L. HOYT AND M. A. SCHEIL,\* MEMBERS A.I.M.E.

(New York Meeting, February, 1937)

ABOUT three years ago eight standard steels were prepared for the cooperative investigation of methods for oxygen analysis, sponsored by the Iron and Steel Division of the American Institute of Mining and Metallurgical Engineers and by the National Bureau of Standards. A preliminary report of the results was made at the annual meeting of the A.I.M.E. in February, 1936.† This report showed the reliability of vacuum-fusion methods and further brought out certain advantages of the fractional vacuum-fusion method. The results obtained by the authors with the latter method will be discussed here, with some comments on the procedure for those who are interested in determinations of gases in steel. Some additional comments are offered on the use of the polarizing microscope for identifying the inclusions in the steel to check and amplify the findings of the fractional vacuum-fusion analysis. For details of the fractional method, see the paper by L. Reeve<sup>1</sup>.

## DEGASSING THE CRUCIBLE

One of the sources of error in vacuum-fusion methods has been the blank gases evolved from the graphite crucible after preliminary outgassing. We have used 1750° C. as the outgassing temperature. This gives a base pressure at that temperature of less than 0.030 mm. after one hour and of 0.004 mm. on dropping the temperature to 1575° C. At lower extraction temperatures the base pressure is 0.001 mm. at 1050° C., 0.002 mm. at 1170° and 0.003 mm. at 1320° C. Because of the size of our induction coil we are limited to this temperature, although it would be advantageous to use 1950° to 2000° C. Hamilton<sup>2</sup>, after outgassing at 1850° C. for 100 min., was able to reach a base pressure of 0.001 mm. for a temperature of 1700° to 1725° C. This would give a blank corresponding to less than 0.00015 per cent O<sub>2</sub> and 0.00005 per cent H<sub>2</sub>. Chipman and Marshall outgas at 2000° C. for one hour by using a special construction

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† A full report was prepared and published later in the year, which includes all the methods used to investigate these steels<sup>19</sup> (see page 246, this volume).

<sup>1</sup> References are at the end of the paper.

and a radiation shield of BeO. On the basis of a 20-gram sample of steel run for 30 min. at 1600° C. their blank corresponds to 0.00125 per cent O<sub>2</sub> and 0.00005 per cent H<sub>2</sub><sup>3</sup>. Norton and Marshall<sup>4</sup> degassed Tungar anodes which were made from Acheson graphite and found at 2150° C. that it is possible to degas graphite so completely that subsequent heating at a higher temperature gives no further gas. They observed that the gas evolved in the range of 1700° to 2200° C. is predominantly nitrogen. A typical analysis of the gas evolved at 2100° C. was given as: H<sub>2</sub> nil, CO 9 per cent, CO<sub>2</sub> 4 per cent, N<sub>2</sub> 87 per cent. It is interesting that they found CO<sub>2</sub> in the gases evolved from this particular graphite at temperatures from 1300° to 2100° C.

We have had certain lots of Acheson graphite that contained small amounts of CO<sub>2</sub> as well as CO, though it is usual to find H<sub>2</sub>, CO and N<sub>2</sub> after outgassing at 1750° C. The particular lot of Acheson graphite used for the cooperative samples gave off no nitrogen in the blank gases for the four separate fractions. A determination of the gases from the one-hour degasification showed only 4 per cent N<sub>2</sub>, which came off during the first half hour. The only blank correction required was for H<sub>2</sub> and CO. Chipman and Marshall find about 40 per cent H<sub>2</sub> and 60 per cent CO in the gases evolved after degasification at 2000° C. From this it is clear that graphite varies in content and analysis of gas and that is one reason we feel that an improvement would be effected by using a higher degassing temperature to eliminate the blank correction. In the work reported here the blank correction amounts to less than 0.002 per cent for oxygen and 0.0003 per cent for hydrogen for a sample run 30 min. at 1575° C., while this could be lowered to about 0.001 per cent and 0.00005 per cent, respectively, by outgassing at 2000° C. The blank gases evolved at lower extraction temperatures, with our outgassing procedure, are negligible, about 0.0006 per cent O<sub>2</sub> and 0.0001 per cent H<sub>2</sub>, so that our results for FeO, MnO and SiO<sub>2</sub> are not vitiated from this source. We would also recommend increasing the size of the sample from 12 grams to at least 25, or even 50, to secure greater accuracy. A low content of gas, like that in well made killed steels, gives a small gas sample of about 3 c.c. While volumes as small as 0.2 c.c. can be analyzed in our Orsat apparatus, the larger sample would give an undoubted advantage.

We have made one other modification here which deserves mention. The graphite crucible originally described by Reeve has been changed slightly to give an inside diameter of  $\frac{9}{16}$  in. and an outside diameter of  $\frac{3}{4}$  in. This increases the clearance between the crucible and the refractory sleeve to  $\frac{1}{8}$  in. This is not so necessary when beryllia is used instead of sillimanite. At the same time the bottom of the crucible has been cut down from a thickness of  $\frac{1}{2}$  in. to  $\frac{1}{4}$  in. Chipman found that radiation shields of BeO give less trouble than other materials and it was at his suggestion that we changed from the original sillimanite. With

these changes we have been able to increase the degassing temperature somewhat and to lower the blank correction, though this was done after the standard samples were run.

### IRON OXIDE AND MANGANESE OXIDE

In Reeve's early work we were not certain that FeO and MnO could be determined separately and he reported the two fractions together, with a statement that one or the other predominated or that one was present only in traces. This distinction was made by following the rate of change of pressure. If FeO was present a rapid gas evolution took place at 1050° C. and the gas was collected until the base pressure was established. Then the temperature was raised to 1150° C. and if a further gas evolution was noted by a distinct and slow rise in pressure, this was collected and called MnO. When there was less than 0.1 c.c. of gas in the first fraction, this was collected with the second fraction and was reported with that in the second fraction and called a trace of FeO. We have modified this procedure with the object of determining FeO and MnO separately, though not without encountering at least apparent difficulties. These are important to an understanding of the errors involved in the separation.

Reeve had shown that the reduction temperatures of FeO and MnO are sufficiently different to justify taking one fraction at 1050° C. for FeO and another at 1170° C. for MnO. These temperatures, along with 1320° and 1570° C. for the reduction of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> in steel by carbon have been confirmed by the reduction of powdered oxides and silicates<sup>5</sup>, and it is felt that with the exception of alumina the reduction goes to over 90 per cent completion. Two points must be considered here to get a proper understanding of possible errors, the failure of the iron-tin alloy to become completely fused at the lower temperature and the possible interference of silicon in upsetting the reactions.

The separation of FeO and MnO has always required close temperature control and frequent careful pressure readings. Samples high in FeO are particularly difficult to handle, especially when the sample is large and the FeO inclusions are massive. The 50 per cent Sn mixture we use does not melt completely until 1137° C., and solidifies at 1120° C., according to some recent determinations of this behavior. High-carbon samples have been observed to be molten at appreciably lower temperatures, while the carburization that comes from the crucible also acts in that same direction. A test of the final regulus, which contained about 6.5 per cent C and 70 per cent Fe, showed that it melted at 1110° C. and solidified at 1093° C. Of course this is not a good test of the melting point of the initial charge because much of the tin is lost during the high-temperature extractions. With a larger graphite crucible than we use it might be feasible to degasify the graphite, lower the temperature to

about 1350° C., drop the tin and outgas at this temperature, then lower the temperature to 1050° C. and drop the sample. The tin would form an 80:20 tin-iron alloy, which would fuse completely at 1050° C.

Another possible source of error during the first two extractions is the metallic silicon content of the steel. If there were an appreciable amount of this element, it would be available for the reduction of FeO and MnO, to lower the determinations for those two constituents and increase the amount of oxygen as silica. We feel that this does not happen with the usual commercial steels and, in fact, if the steel is properly made the silicon addition would insure the absence or practical absence of FeO. As a special test of this point we are fortunate in having Reeve's data on a badly oxidized gray iron. He reported 0.047 per cent O<sub>2</sub> as FeO and MnO, of which much was FeO, though the iron contained 3.0 per cent C, 1.7 per cent Si and 0.4 per cent Mn. The oxygen as silica was only 0.007 per cent, which indicated that no appreciable interference occurred because of the presence of metallic silicon. Our microscopic examination with polarized light indicated the presence of some such small amount of silica, and also showed appreciable amounts of FeO in the cast iron. This oxidized condition of the iron was associated with definitely inferior quality and we believe that these findings suggest possibilities in the use of these methods for studying cast iron which would more than likely yield valuable results.

### METALLIC VAPORS

A second point of great importance in vacuum-fusion analysis is the interference of vapors of manganese, aluminum, etc., which are distilled off the molten sample. It has been clearly shown that the presence of such vapors or their condensates in the colder portions of the furnace give oxygen values that are too low. In some recorded cases this error is so great that the results are entirely vitiated. Manganese is the most serious offender, as that element is volatile at the extraction temperatures and is likely to occur in commercial steels in amounts that produce a marked effect. Furthermore, it appears that with conditions apparently the same two observers may secure quite different results.

Vacher and Jordan<sup>6</sup> have paid special attention to this interference of manganese in "total oxygen" determinations, to which these comments apply specifically. At 1600° C. a substantial portion of the manganese may be distilled off, and they suggest that the CO evolved from the reduction of the oxides in the sample would be expected to react according to  $\text{Mn} + \text{CO} = \text{MnO} + \text{C}$ . This would lower the amount of CO recovered during the extraction. This effect became noticeable at about 0.24 per cent Mn when using a crucible containing one residue of the same steel. It should be noted that manganese in the

sample distills off to cause a lowering of the oxygen value if successive samples are allowed to accumulate in the crucible. By operating at lower pressures and removing the CO gas very rapidly from the furnace, the manganese effect can be very largely avoided.

More recently this point has been critically analyzed by Thanheiser<sup>7</sup>, who reported investigations made in the Kaiser Wilhelm Institut für Eisenforschung. The results show that finely divided manganese reacts with pure CO in the temperature range 400° to 750° C. and at pressures of 60 mm. and less to form MnO and precipitate carbon. In addition, it was found that CO was absorbed even at room temperatures, but at temperatures below 300° C. no carbon was precipitated. Further experiments were made to decide whether it is possible by intensive cooling to eliminate the reaction between CO and Mn. CO was admitted during volatilization of Mn in such a way that the pressure never exceeded 1 mm. Hg. In these tests absorption of CO occurred even when the tube containing the Mn was intensively water-cooled. The investigation did not distinguish between a reaction of the Mn vapor with the CO and a reaction after condensation of the Mn on the inner surface of the tube. Further tests were made in which a sample of Bessemer steel with 0.023 per cent O<sub>2</sub> was melted with Mn in vacuo to give a manganese content in the charge of about 2.4 per cent. By means of a special apparatus, a graphite bell was installed in the furnace tube, which could be raised or lowered, so as to be cooled or heated, without breaking the vacuum. By this method these investigators studied the influence of cooling or heating the surface upon which the manganese vapors condense. The tests verified the earlier results with manganese coatings and pure CO gas. The greater the cooling effect on the graphite, the greater was the quantity of CO retained by the manganese deposit, while heating the manganese deposit to a higher temperature gave normal oxygen determinations for the sample.

This discussion of the interference of manganese, either as a vapor or as a condensed finely divided deposit, upon the total oxygen value by the total vacuum-fusion method brings up a similar question with the fractional method. The fractional method, by reason of the slow reduction of the different oxides at temperatures of 1050°, 1170°, 1320° and 1570° C., offers more opportunity for manganese interference than the total oxygen method. The latter is usually carried out in about 20 min. at 1600° C., while the fractional method involves holding the sample at 1320° C. for ½ to 1 hr. and a similar period at 1570° C. However, it appears that tin not only lowers the melting point of the sample but also minimizes or completely inhibits the manganese effect, which undoubtedly is the reason that our results for total oxygen, secured by adding up the separate fractions, agree with the total oxygen determined by the regular vacuum-fusion procedure. About 50 per cent of the tin is volatilized during the



fractional vacuum fusion, and we presume it alloys with the metal vapors and lowers their reactivity with carbon dioxide.

To illustrate the effect of tin on the recovery of oxygen from a high-manganese steel, we will discuss steel No. 2 of the cooperative samples, which contains 1.15 per cent Mn. The range of oxygen values reported by 13 investigators using the vacuum-fusion method was 0.010 to 0.018 per cent. Though 54 of these values were between 0.010 and 0.016 per cent oxygen, the "selected" range for this steel was taken as 0.012 to 0.018 per cent and represents the difficulties involved in determining the oxygen in this high-manganese steel. Furthermore, 0.014 to 0.018 per cent oxygen was thought to be probably the best range, with 0.017 per cent as the selected or preferred oxygen value for this steel. Our results with steel No. 2 show a total oxygen of 0.014 per cent, and, we feel, demonstrate the assistance of tin in the recovery of oxygen in a high-manganese steel.

As far as we have been able to determine, the practice of using a fresh graphite crucible and a clean quartz furnace tube (cleaned in hydrochloric acid after each determination) for each fractional run has given total oxygen values (obtained by adding the oxygen of the four fractions; for example, FeO, MnO, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>) comparable to those obtained by the "total oxygen" method described by Vacher and Jordan<sup>6</sup>.

In addition to manganese the only other metallic vapors that might interfere in determinations of the oxygen content of the carbon steels are those of aluminum and silicon. Diergarten<sup>8</sup> has observed a similar interference by aluminum when more than 0.3 per cent Al was present, but this is well above the normal content. Vacher and Jordan could not find any interference by metallic silicon up to 4.0 per cent<sup>6</sup>.

#### FRACTIONAL NITROGEN

So far we have been discussing oxygen and the factors that affect complete oxygen removal from steel when heated in vacuo. We have now to consider nitrogen and the type of information on this element that is obtained by the fractional vacuum method. It was rather early recognized that nitrogen occurs in commercial steel and it was strongly suspected that nitrogen had certain specific effects on the properties and behavior of the material, mostly harmful effects. Chemical methods were developed for the determination of the (total) nitrogen and it has usually been with that figure that the behavior of the steel has been correlated.

On the other hand, it has been recognized that other nitrides may occur in steel, or at least that nitrogen can occur in some association other than in simple solution in or combination with iron. Dr. C. M. Johnson, for example, has introduced a wet extraction method to distinguish soluble and insoluble nitrides in stainless steel as a step in this direction<sup>9</sup>. It

was also with the thought that the elements that form the more stable nitrides should improve the hardness of nitrified steel surfaces and lower the temperature of nitrifying that Fry added such elements as aluminum to steel. It is our purpose to indicate how the fractional vacuum-fusion procedure can contribute to a better understanding of this problem. The justification for this discussion, or its basis, is the presence of nitrogen in varying amounts in the four fractions, bearing in mind that the pressure at the end of each fractional extraction dropped to the base pressure for the respective temperature. The first inference is that the various nitrogen fractions occur in the steel in combination with different elements as different molecular species, though they may be dissolved to some extent in the different oxides to be released when the oxide is reduced. The latter is at least a possible source of some of the nitrogen found.

Our first and most serious consideration will be given to the thermal decomposition of a series of nitrides with increasing stability, and requiring higher temperatures for decomposition.

Recently Fry<sup>10</sup> has shown the disintegration of various nitrides by heating in vacuo at temperatures up to 1000° C. Iron nitride prepared by him starts to decompose at 400° C. and ends at 800° C., showing a maximum at 600° C. The residue analyzed 0.005 per cent N<sub>2</sub>. Manganese nitride when treated in the same manner begins to decompose at 500° C. and is not completed at 1000° C. The residue analyzed 1.9 per cent N<sub>2</sub>. Aluminum nitride does not decompose at any temperature below 1100° C. Tschischewski<sup>11</sup> shows from experiments that silicon reacts with gaseous nitrogen at 1400° to 1500° C. to form a nitride, Si<sub>2</sub>N<sub>3</sub>, which dissociates at temperatures above 1400° C. in vacuo. According to Jean Rieber<sup>12</sup>, aluminum nitride decomposes above 1400° C. Other investigators have reported that this nitride does not dissociate at 1750° C. but Jordan and Eckman<sup>13</sup> prepared silicon, aluminum, titanium, zirconium, chromium and vanadium nitrides by heating powders of these metals at 1300° to 1350° C. in nitrogen and in nitrogen and hydrogen. Nitrified samples, 0.05 to 0.10 grams, were heated to 1650° C. in vacuo with 20 to 30 grams of electrolytic iron previously fused in graphite in vacuo. The results show that these nitrides were successfully disintegrated by vacuum-fusion procedure.

While this evidence is not conclusive, it supports our present opinion that the nitrogen found in these four fractions is associated with some metals besides iron. Tentatively we like to call the nitrogen in the 1050° and 1170° C. fractions iron nitride and manganese nitride, and the nitrogen in the 1320° and 1570° C. fractions silicon and aluminum nitrides.

There is much evidence in the literature<sup>14</sup> to show that the ordinary amounts of nitrogen in weld metal can be precipitated out as nitride plates by slowly cooling a sample from above the upper critical temperature. It now seems likely that this nitrogen must be associated as iron

nitride in order to form the characteristic "nitride needles." Nitrides other than iron nitrides such as we obtain in the fractions at 1320° and 1570° C. do not precipitate "nitride needles" when given a "nitride anneal."

TABLE 1.—*Nitrogen Determinations*

Fraction at	Form	Gases Determined as Nitrogen, Per Cent			
		Bessemer Steel	Weld A	Weld B	Weld C
1050° C. }	Fe and.....	0.001	0.022	0.009	0.001
1170° C. }	Mn nitrides.....	0.001	0.002	0.000	0.000
1320° C.	Possibly Si nitride.....	0.004	0.012	0.010	0.004
1570° C.	Possibly Al nitride.....	0.009	0.013	0.017	0.009
	Total nitrogen.....	0.015	0.049	0.036	0.014
	Nitride needles.....	No	Yes	No	No

This sample of Bessemer steel did not show nitride needles after the annealing treatment though its "total" nitrogen content is commonly assumed to be high enough, and neither does the weld metal C. In both the iron nitride, or first fraction nitrogen, is low.

Weld metal A contains high nitrogen in the first fraction and the annealed microsection shows the characteristic needles. Weld metal B, with only 0.009 per cent N<sub>2</sub> in the first and second fraction but with about the same amount in the third and fourth fractions as weld A, does not show nitride needles in the microsection after being given the same heat-treatment that brought them out in weld A.

The nitrogen determined by wet chemical methods does not distinguish iron nitride from other possible combinations of nitrogen and in this respect the full significance of the determination is lost. Nitrogen determinations by the distillation method compare favorably with the total nitrogen by vacuum fusion. On weld metal A the total nitrogen by distillation was reported as 0.053 per cent.

#### MICROSCOPIC EXAMINATION OF STEELS

After completing the fractional vacuum-fusion analyses of the eight cooperative samples, each sample was examined for inclusions, with the metallurgical microscope using plain light and polarized light. The authors have described their equipment and technique in a previous publication<sup>15</sup>. A longitudinal and a transverse cross section of each sample was prepared for metallographic examination, by the automatic polishing machine. On examining these two sections we found that the longitudinal specimen was best suited to a study of the inclusions.

Our regular procedure is first to observe the degree of cleanliness, size, distribution and color of the visible inclusions. After this examination the same field is observed with reflected polarized light, to distinguish opaque from optically active inclusions. Then, by rotation of the specimen about the optical axis, the bright inclusions are further classified as glassy or transparent crystalline, and are more closely characterized by means of their coloring and optical effects.

The use of reflected polarized light with crossed nicols establishes the combination of many of the oxide inclusions and when used in conjunction with the fractional oxide analysis gives a more complete understanding of the oxide inclusions.

*Steel No. 1. Low-carbon Rimming Steel.*—Our sample shows a very complex stringer inclusion 0.4 mm. below the rolled surface. This inclusion shows fine networks of FeS separating MnO·MnS. Judging from the optical activity of this inclusion in reflected polarized light, we conclude that parts of the constituents that appear dark as observed with plain reflected light in this complex inclusion contain SiO<sub>2</sub>. The brown color of the optically active inclusions with crossed nicols suggests that this is a silicate contaminated with FeO and MnO by reason of the transmitted color. Near the center of the longitudinal cross section our sample shows a very interesting complex, broken stringer. The size of several of these permitted us to give this inclusion a thorough examination. In plain reflected light we observe in many of these inclusions well formed individual crystals of nearly the same color as the matrix. Our automatic polisher did not show up a difference in hardness between the crystals and their matrix, but a scratch test made with a diamond point showed the crystals to be somewhat harder than the matrix. Reflected polarized light with crossed nicols shows the whole inclusion in many cases to be optically active. Upon rotation of the specimen the individual crystals show marked birefringence and exhibit brilliant reflected colors. Occasionally the matrix is bright, but usually shows a reddish brown color. From our observations of these inclusions the individual crystals appear to be a refractory iron-chromium-aluminate in a matrix of silicate contaminated with other oxides. The other inclusions present were observed as opaque inclusions and are identified as fine stringers of MnO·MnS. In a few of the small stringers we observed rounded silicate inclusions. All that we observed were contaminated to the extent that they showed colors of some other oxide constituent. We suspect that the complex iron-chromium-aluminate present near the center of the rolled bar may be the result of some furnace or ladle refractory carried into the ingot mold during pouring.

*Steel No 2. Medium-carbon High-manganese Silicon-killed Steel.*—Most of the inclusions in the section prepared for this steel were found to be MnO·MnS stringers of a light gray color in plain illumination. There

are a few inclusions of a darker gray color, though similar in size to the lighter color MnO·MnS stringer inclusions, which show optical activity and are probably manganese silicate stringers. From our analysis we expected to find more of these glassy manganese silicates, and the only reason that we can give is that some large silicate inclusions were missed by the section examined. This is substantiated by the time of reaction that was necessary to reduce the third fraction, SiO<sub>2</sub>, in this sample. Instead of the usual 30-min. period, which is about the normal time required to reduce SiO<sub>2</sub> in silicon-killed steels, this particular sample required about one hour to reach the normal base pressure for 1320° C. Similar results have been experienced with weld-metal samples in which large silicates occurred, and it is not unusual on some samples that we have analyzed to see large inclusions carried to the surface of the bath. There they appear to boil while the gas pressure in the furnace indicates that reduction is proceeding slowly.

*Steel No. 3. Bessemer Screw Stock; Rimming Steel.*—Our sample shows a large amount of opaque stringer inclusions with reflected polarized light and crossed nicols. These opaque inclusions are mainly MnO·MnS stringers. We observed a few long optically active stringers of impure silicates under the rolled surface of the bar and also through the central portions of the bar. Frequently we observed short stringers of MnO·MnS with optically active tails, which again we would identify as silicates. We did not observe any characteristic segregations of alumina in our examination of this steel but we expect that the alumina is associated with the silicate. We are not able to identify it with our present technique.

The fractional vacuum-fusion analysis of this steel shows that not more than 0.002 per cent nitrogen occurs as iron nitride, though there is an appreciable amount associated with the deoxidizers. After giving this sample a heat-treatment to precipitate iron nitride, we did not observe any needlelike constituent.

*Steel No. 4. Low-carbon Special Aluminum-killed Steel.*—Our sample is very clean and shows a few fine sliverlike inclusions, all very small. There are no inclusions that show any optical activity with polarized light, from which we conclude that any alumina dispersion must be sub-microscopic. This is a fine-grained steel by the McQuaid-Ehn test.

*Steel No. 5. Low-carbon Silicon-killed Steel.*—The results with this steel with polarized light agreed very well with the results of the fractional vacuum-fusion analysis. We observed small stringer inclusions in our sample and identified many of them as manganese silicates with some additional opaque inclusions of MnO·MnS. The time for the third fraction of this steel indicates that it does not have such large inclusions as steel No. 2; the SiO<sub>2</sub> was completely reduced in less than 30 min. The tabulated data show that both steels contain about the same amount of oxygen as silica.

*Steel No. 6. Medium-carbon Silicon-killed Steel.*—This steel has the appearance of a high-quality forging steel. The examination with polarized light confirmed the results of the fractional vacuum-fusion analysis. Tiny stringer inclusions predominated in our sample and were identified as MnO-MnS. A few manganese silicate stringers were observed, partly as tails on a few of the elongated MnO-MnS inclusions.

TABLE 2.—Results of Tests by Fractional Vacuum Fusion

STEEL No. 1. LOW-CARBON RIMMING STEEL							
Chemistry: C, 0.03; Mn, 0.31; P, 0.011; S, 0.036; Si, 0.004; Cr, 0.004; V, 0.001							
Oxygen by Int. Coop. Report: Range, 0.016 to 0.020 per cent O <sub>2</sub> . Selected value, 0.018 per cent O <sub>2</sub>							
Gases by Fractional Vacuum Fusion: Sample Weight 10.95 grams							
Temperature of Fraction, Deg. C.	Oxygen as	Weight Per Cent				Volume at Normal Temp. and Pressure, c.c.	Time for Reduction, Min.
		Oxide	O <sub>2</sub>	N <sub>2</sub>	H <sub>2</sub>		
1050	FeO	0.009	0.002	0.001	0.0003	1.10	60
1170	MnO	0.058	0.013	0.000	0.0001	2.29	30
1320	SiO <sub>2</sub>	0.002	0.001	0.000	0.0002	0.71	30
1570	Al <sub>2</sub> O <sub>3</sub>	0.007	0.004	0.002	0.0000	1.32	30
Total . . . . .	.....	0.076	0.020	0.003	0.0006	5.42	

STEEL No. 2. MEDIUM-CARBON HIGH-MANGANESE SILICON-KILLED STEEL

Chemistry: C, 0.42; Mn, 1.15; P, 0.020; S, 0.025; Si, 0.26; Cr, 0.022; V, 0.001							
Oxygen by Int. Coop. Report: Range, 0.012 to 0.018 per cent O <sub>2</sub> . Selected value, 0.017 per cent O <sub>2</sub>							
Gases by Fractional Vacuum Fusion: Sample Weight 10.70 grams							
Temperature of Fraction, Deg. C.	Oxygen as	Weight Per Cent				Volume at Normal Temp. and Pressure, c.c.	Time for Reduction, Min.
		Oxide	O <sub>2</sub>	N <sub>2</sub>	H <sub>2</sub>		
1050	FeO	0.005	0.001	0.002	0.0002	1.00	45
1170	MnO	0.027	0.006	0.000	0.0002	1.31	45
1320	SiO <sub>2</sub>	0.011	0.006	0.000	0.0002	1.54	50
1570	Al <sub>2</sub> O <sub>3</sub>	0.002	0.001	0.001	0.0002	1.04	30
Total . . . . .	.....	0.045	0.014	0.003	0.0008	4.89	

*Steel No. 7. Open-hearth Iron; Rimming.*—Both microsections of this sample show only opaque inclusions with reflected polarized light and crossed nicols. With plain reflected light these inclusions appear as globular or semi-elongated globular shapes, and all are single-phase inclusions identified as FeO. We were not able to observe any optically active inclusions such as silicates or aluminates.

*Steel No. 8. Low-carbon Special Steel; Aluminum-killed.*—Both microspecimens show a segregation of inclusions appearing near the center of the bar. These inclusions are fine and appear in bands running longitudinally through the bar. With crossed nicols we observed a few inclusions with the optical cross, characteristic of  $\text{SiO}_2$  and a great many more inclusions that show optical activity. From the appearance, difficulty in

TABLE 2.—(Continued)

## STEEL No. 3. BESSEMER SCREW STOCK, RIMMING STEEL

Chemistry: C, 0.12; Mn, 0.72; P, 0.101; S, 0.168; Si, 0.024; Cr, 0.006; V, 0.004

Oxygen by Int. Coop. Report: Range, 0.014 to 0.020 per cent  $\text{O}_2$ . Selected value, 0.017 per cent  $\text{O}_2$

Gases by Fractional Vacuum Fusion: Sample Weight 10.52 grams

Temperature of Fraction, Deg. C.	Oxygen as	Weight Per Cent				Volume at Normal Temp. and Pressure, c.c.	Time for Reduction, Min.
		Oxide	$\text{O}_2$	$\text{N}_2$	$\text{H}_2$		
1050	FeO	0.007	0.002	0.001	0.0002	0.92	45
1170	MnO	0.049	0.011	0.001	0.0002	2.28	45
1320	$\text{SiO}_2$	0.007	0.004	0.004	0.0002	1.84	60
1570	$\text{Al}_2\text{O}_3$	0.010	0.004	0.009	0.0000	1.65	30
Total.....	.....	0.073	0.021	0.015	0.0006	6.69	

## STEEL No. 4. LOW-CARBON SPECIAL ALUMINUM-KILLED STEEL

Chemistry: C, 0.17; Mn, 0.65; P, 0.014; S, 0.029; Si, 0.09; Cr, 0.008; V, 0.001

Oxygen by Int. Coop. Report: Range, 0.001 to 0.004 per cent  $\text{O}_2$ . Selected value, 0.002 per cent  $\text{O}_2$

Gases by Fractional Vacuum Fusion: Sample Weight 11.17 grams

Temperature of Fraction, Deg. C.	Oxygen as	Weight Per Cent				Volume at Normal Temp. and Pressure, c.c.	Time for Reduction, Min.
		Oxide	$\text{O}_2$	$\text{N}_2$	$\text{H}_2$		
1050	FeO	0.000	0.000	0.000	0.0001	0.27	20
1170	MnO	0.000	0.000	0.000	0.0001	0.18	15
1320	$\text{SiO}_2$	0.002	0.001	0.000	0.0001	0.54	30
1570	$\text{Al}_2\text{O}_3$	0.008	0.004	0.002	0.0000	1.34	30
Total....	.....	0.010	0.005	0.002	0.0003	2.33	

polishing without fracturing, and the optical activity of these small inclusions, they are probably aluminum silicates such as Herty<sup>16</sup> describes. Our oxygen analysis indicates that there is twice as much oxygen as silica as there is oxygen as alumina. Other methods, principally wet extraction methods, indicate the opposite. We have run check

analyses on this sample and have obtained identical results regarding the amount of oxygen as silica and alumina, and the total oxygen of our fractions checks well with the total oxygen by vacuum fusion. Our examination with crossed nicols does show positive evidence of the occurrence of some silica in the inclusions but we are not able to distinguish ferrous aluminate and aluminum silicate by our present technique. We

TABLE 2.—(Continued)

## STEEL NO. 5. LOW-CARBON SILICON-KILLED STEEL

Chemistry: C, 0.22; Mn, 0.45; P, 0.020; S, 0.042; Si, 0.14; Cr, 0.020; V, 0.001

Oxygen by Int. Coop. Report: Range, 0.007 to 0.011 per cent  $O_2$ . Selected value, 0.009 per cent  $O_2$

Gases by Fractional Vacuum Fusion: Sample Weight 11.11 grams

Temperature of Fraction, Deg. C.	Oxygen as	Weight Per Cent				Volume at Normal Temp. and Pressure, c.c.	Time for Reduction, Min.
		Oxide	$O_2$	$N_2$	$H_2$		
1050	FeO	0.000	0.000	0.000	0.0001	0.27	15
1170	MnO	0.018	0.004	0.001	0.0001	1.07	45
1320	$SiO_2$	0.013	0.007	0.000	0.0003	1.52	30
1570	$Al_2O_3$	0.002	0.001	0.001	0.0000	0.54	15
Total....	.....	0.033	0.012	0.002	0.0005	3.40	

## STEEL NO. 6. MEDIUM-CARBON SILICON-KILLED STEEL

Chemistry: C, 0.43; Mn, 0.47; P, 0.014; S, 0.027; Si, 0.20; Cr, 0.012; V, 0.001

Oxygen by Int. Coop. Report: Range, 0.005 to 0.008 per cent  $O_2$ . Selected value, 0.007 per cent  $O_2$

Gases by Fractional Vacuum Fusion: Sample Weight 11.25 grams

Temperature of Fraction, Deg. C.	Oxygen as	Weight Per Cent				Volume at Normal Temp. and Pressure, c.c.	Time for Reduction, Min.
		Oxide	$O_2$	$N_2$	$H_2$		
1050	FeO	0.000	0.000	0.000	0.0001	0.31	30
1170	MnO	0.013	0.003	0.000	0.0001	0.70	30
1320	$SiO_2$	0.004	0.002	0.000	0.0001	0.62	30
1570	$Al_2O_3$	0.002	0.001	0.003	0.0000	0.76	30
Total....	.....	0.019	0.006	0.003	0.0003	2.39	

believe, however, that there is small possibility of ferrous aluminate, if it were present, escaping reduction at 1050°, 1170° and 1320° C. Another alternative is that finely dispersed aluminum silicate may be reduced entirely at the third fraction. The alumina so reduced would appear in the third fraction. G. T. Motok<sup>17</sup> has recently discussed some results obtained by fractional vacuum-fusion analysis of commercial steels. In



this work he has reported oxygen as aluminum silicate in a fraction at 1515° C. between silica at 1320° and alumina at 1650° C. (Motok states that if the alumina particles are fine, a complete reduction can be made at 1570° C.). This aluminum silicate fraction is new and it may well be that steel No. 8 contains this type of inclusion, and that it is responsible for our results on silica and alumina. Obviously, the examination with polarized light would be capable of giving strong supporting evidence.

TABLE 2.—(Continued)

## STEEL No. 7. OPEN-HEARTH IRON, RIMMING

Chemistry: C, 0.016; Mn, 0.02; P, 0.011; S, 0.022; Si, 0.003; Cr, 0.009; V, 0.001

Oxygen by Int. Coop. Report: Range, 0.100 to 0.110 per cent O<sub>2</sub>. Selected value, 0.106 per cent O<sub>2</sub>

Gases by Fractional Vacuum Fusion: Sample Weight 13.22 grams

Temperature of Fraction, Deg. C.	Oxygen as	Weight Per Cent				Volume at Normal Temp. and Pressure, c.c.	Time for Reduction, Min.
		Oxide	O <sub>2</sub>	N <sub>2</sub>	H <sub>2</sub>		
1050 } 1170 }	FeO	0.449	0.100	0.003	0.0000	20.37	240
1320	SiO <sub>2</sub>	0.006	0.003	0.001	0.0001	1.25	30
1570	Al <sub>2</sub> O <sub>3</sub>	0.000	0.000	0.000	0.0000	0.31	30
Total....	.....	0.455	0.103	0.004	0.0001	21.93	

## STEEL No. 8. LOW-CARBON SPECIAL STEEL, ALUMINUM-KILLED

Chemistry: C, 0.20; Mn, 0.45; P, 0.014; S, 0.033; Si, 0.03; Cr, 0.012; V, 0.001

Oxygen by Int. Coop. Report: Range, 0.015 to 0.019 per cent O<sub>2</sub>. Selected value, 0.017 per cent O<sub>2</sub>

Gases by Fractional Vacuum Fusion: Sample Weight 10.81 grams

Temperature of Fraction, Deg. C.	Oxygen as	Weight Per Cent				Volume at Normal Temp. and Pressure, c.c.	Time for Reduction, Min.
		Oxide	O <sub>2</sub>	N <sub>2</sub>	H <sub>2</sub>		
1050	FeO	0.000	0.000	0.000	0.0001	0.36	30
1170	MnO	0.009	0.002	0.000	0.0002	0.58	30
1320	SiO <sub>2</sub>	0.017	0.009	0.001	0.0001	2.32	60
1570	Al <sub>2</sub> O <sub>3</sub>	0.011	0.005	0.002	0.0000	1.69	30
Total....	.....	0.037	0.016	0.003	0.0004	4.95	

If we were able to take these inclusions out of the steel sample and study them in thin section or dispersed in a liquid of the same index of refraction, by the method that has been described by Larsen and Berman<sup>18</sup>, we should be able to identify them positively by their index of refraction and

birefringence and in this manner settle the discussion regarding their hot reduction.

## RESULTS OF FRACTIONAL VACUUM-FUSION ANALYSIS

Table 2 gives our complete results on the cooperative samples.

### SUMMARY

In this paper we have presented our results for the eight samples used for the cooperative study of methods for determining oxygen in steel sponsored by the Iron and Steel Division of the A.I.M.E. and by the National Bureau of Standards. Some comments are offered to help clarify and improve the fractional method. In particular, we have discussed fractional nitrogen to indicate the status of such determinations, and we have shown how the polarizing microscope may be used to assist in the study of the oxides in the steel.

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## DISCUSSION

(C. H. Hertý, Jr., *presiding*)

S. MARSHALL AND J. CHIPMAN,\* Middletown, Ohio (written discussion).—This paper is a timely supplement to the cooperative report (pp. 246 to 291), in that it describes the method by which the only fractional vacuum-fusion results reported were obtained. In our experience with the fractional method, ingot iron and low-carbon steel do not dissolve in liquid tin at 1050°. We hesitate, therefore, to accept any conclusions whatsoever regarding the source of the oxygen in this fraction. Notwithstanding this point of uncertainty, the results obtained by this method, both for FeO and for MnO, are more in keeping with the melting practice and inclusion content than are those of any other method.

The authors' observation that the error caused by distillation of manganese is minimized by the presence of tin constitutes a most valuable contribution to the development of the vacuum-fusion method. This source of error has been a stumbling block to many investigators, and in the past has been overcome only by the use of exceptionally high-speed vacuum pumps. We have obtained a full confirmation of this observation by determinations of the total oxygen content of steel No. 2. This steel contains 1.15 per cent Mn, which is far above the range for which our apparatus was designed. Without tin we found 0.011 to 0.013 per cent O<sub>2</sub>, with tin 0.017 per cent. Similarly with sample No. 4, containing 0.65 per cent Mn, we found 0.001 without tin, and 0.0025 per cent O<sub>2</sub> when tin was employed.

As regards the blank correction, it is hard to conceive of a correction at 0.001 mm. being negligible and one at 0.004 mm. not being excessive. Most operators strive for a pressure of 0.001 mm. or less at 1600° C. in running "total" oxygen, and do not have negligible blanks even for fairly short degassing periods, while in some of the cases reported the first, or 1050° C., fraction is degassed from 30 min. to 1 hr., and sample No. 7 was degassed 4 hr.

In our opinion the nitrogen found in the blank gas after thorough outgassing comes from small leaks in wax seals or other parts of the system. We have used several different lots of Acheson graphite in the same furnace without finding any nitrogen in the blank. The discussion on fractional nitrogen is the first attempt to estimate the amounts of various nitrides that has come to our attention. It seems, however, that the temperatures of dissociation as reported would overlap so much that a sharp differentiation of the nitrides would be impossible. The supposition that the nitrogen of the final fraction comes from aluminum nitride ought to be capable of experimental verification or disproof by an accurate determination of aluminum. If the nitride is AlN, 0.01 per cent N is associated with 0.015 per cent Al, which is rather high either for weld metal or for Bessemer steel.†

J. H. SCAFF,† New York, N. Y.—It is our practice in carrying out an oxygen determination by the vacuum-fusion method to measure the blank correction both before and after the oxygen determination itself, in order to be certain that no extrane-

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\* Associate Director, Research Laboratories, American Rolling Mill Co.

† Bell Telephone Laboratories.

ous factors enter during the analysis. We have carried out only a few experiments using the fractional procedure, but in these we noted that a rather large amount of tin was vaporized and subsequently deposited on the radiation screen and silica furnace tube during the determination of the  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  fractions. The blank corrections measured subsequent to these determinations were substantially larger than the empty-crucible values, indicating that the tin deposit in some manner increased the evolution of gas from the various parts of the furnace, perhaps by promoting the reduction of refractory parts by carbon. I should like to ask Dr. Hoyt whether he has observed this effect and whether special precautions are necessary to minimize the influence of vaporized tin on the determination.

S. L. HOYT AND M. A. SCHEEL (written discussion).—It is gratifying to have confirmation by Messrs. Marshall and Chipman of the assistance of tin in the recovery of oxygen in the high-manganese steel. The remainder of their discussion relates to points that might be classed as "uncertainties" of the fractional method. We are fully aware of the points raised and it was with the realization that such points can be cleared up only by checks obtained from other and reliable means that we have examined our samples by polarized light and in other ways. One powerful reason for our participating in this cooperative investigation was the opportunity it provided to compare our results with others. On that account we note with approval the remark regarding the uncertainty of FeO and MnO by the fractional method that the results we report "are more in keeping with the melting practice and inclusion content than are those of any other method." It is experience such as we mention here that gives us confidence in our FeO and MnO determinations, in spite of the

TABLE 3.—*Blank Gases in Grams*<sup>a</sup>

	Results with New Tin 12.29 Grams	Temperature of Fractions, Deg. C.	Results with Old Tin 10.24 Grams
H <sub>2</sub> .....	0.000012	1050 and 1170	0.000016
O <sub>2</sub> .....	0.000032		0.000050
H <sub>2</sub> .....	0.000015	1320	0.000024
O <sub>2</sub> .....	0.000064		0.000064
H <sub>2</sub> .....	0.000031	1570	0.000032
O <sub>2</sub> .....	0.000185		0.000388

<sup>a</sup> After outgassing graphite crucible at 1720° C. for one hour.

criticism that the sample does not melt completely in the first fraction. Even so, we feel the point is well taken and in our paper we suggest a method for securing fusion.

We do not agree with their opinion that the nitrogen found in the blank gas after thorough outgassing comes from small leaks in the system. If this were entirely true, then free oxygen would also be present. Our standard practice in making gas analyses of the blanks and fractions from the sample is to determine the presence of free oxygen by passing the diluted gas sample through alkaline pyrogallol. Leaks that may be detected in this manner are rarely encountered.

Coming now to the comments on fractional nitrogen, while we have suggested that the nitrogen in the third and fourth fractions is associated with silicon and aluminum, we do not believe that this is always present as a definite compound such as AlN would suggest. We have pointed out in the paper that nitrogen could be

dissolved in some of the different oxides. We sincerely hope that investigators in the future will be able to take up this method and carefully work out all the details.

Replying to Mr. Scaff: as far as we have been able to determine, the vapors or condensate of tin do not react with the furnace refractory to cause additional gas evolution. We have noted, on certain lots of C.P. stick tin, that the blank gases in the fourth fraction at 1570° C. for  $\text{Al}_2\text{O}_3$ , were slightly increased.

At one time we ran a series of blanks on graphite crucibles from the same lot, using two different lots of tin. After outgassing, the tin was dropped in the evacuated crucible at 1050° C. and the gases collected in the regular manner from each fraction and analyzed.

Table 3 shows the blank gases at the different fraction temperatures for  $\frac{1}{2}$ -hr. periods of evacuation for these two different samples of tin.

The differences in the blank gases are mainly in the fourth fraction. The increase in hydrogen and oxygen using the old tin as compared to the new material results in 0.000018 gram of hydrogen and 0.000239 gram of oxygen when comparison is made on the basis of  $\frac{1}{2}$ -hr. fractions at 1050°, 1170°, 1320° and 1570° C.

A total vacuum fusion of the old tin was made at 1570° C. and the gases determined on about a 10-gram sample. Our analysis showed 0.000020 gram of hydrogen and 0.00023 gram of oxygen, which agrees very well with the increased yield of blank gases as determined by the separate fractions.

It is quite likely that samples of C.P. stick tin can vary in oxygen content, and we have found it necessary to use a material that has a negligible oxygen content. It is for this reason that we recommend dropping the tin, to be alloyed with the sample, separately after the high-temperature outgassing, so that any blank resulting from gases in the tin can be pumped off before the determination of the gases in the steel sample.

## Effect of Temperature upon Interaction of Gases with Liquid Steel

BY JOHN CHIPMAN,\* MEMBER A.I.M.E. AND A. M. SAMARIN†

(New York Meeting, February, 1937)

It has been long known that the gas evolved during the boil in the open-hearth furnace is mainly carbon monoxide associated with smaller quantities of other gases. A number of attempts have been made to determine the precise effects of carbon and oxygen content of the bath, and of other factors, such as temperature, upon the evolution of carbon monoxide. In his investigation of the carbon-iron oxide product in liquid steel, Herty<sup>1</sup> showed that the value of this product at equilibrium could be approximated by plotting the value of the product observed in open-hearth reactions against rate of carbon elimination, and extrapolating to zero rate. The results of this study showed a slight but definite effect of temperature upon the carbon-iron oxide reaction.

Experimental studies of the evolution of gases from rimming-steel ingots have not yet attained the degree of precision necessary for an exact understanding of the effects of pouring temperature, carbon content, and iron oxide in the metal upon the composition of these gases. Klinger<sup>2</sup> showed that the gas consists mainly of carbon monoxide, and that considerable variation in its composition occurs during the solidification of the ingot. In order that these variations may be understood in their proper relationship to the progress of solidification of the ingot and the segregation that accompanies solidification, it is essential to have a knowledge of the condition of equilibrium in the several chemical reactions by which the gases are being formed. It is also necessary to understand the effects of temperature upon the equilibria, and further, to know the manner in which the temperature of the liquid metal within the ingot changes as the skin of the ingot is being built up.

The reactions in which we will be chiefly interested are those involving in the one case the oxides of carbon, and in the other case steam and

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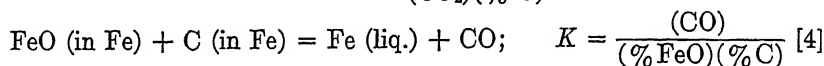
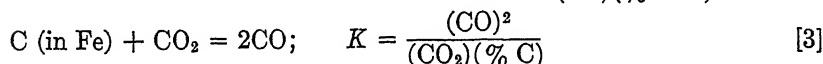
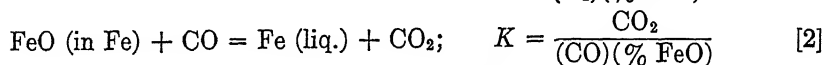
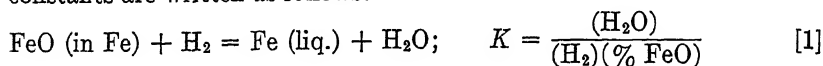
The experimental work reported in this paper was carried out in the laboratories of the Department of Chemical and Metallurgical Engineering, University of Michigan, Ann Arbor. The authors express their appreciation to Prof. A. H. White, Chairman of the Department, for the facilities of the laboratory. Manuscript received at the office of the Institute Nov. 30, 1936.

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† Director, Research Department, Moscow Institute of Steel, Moscow, U. S. S. R.

<sup>1</sup> References are at the end of the paper.

hydrogen, with iron oxide and carbon in the liquid metal. The reactions as they occur in unalloyed liquid iron, and their respective equilibrium constants are written as follows:



An experimental study by Vacher and Hamilton<sup>3</sup> of the reaction by which iron oxide and carbon are formed in liquid iron from carbon monoxide and carbon dioxide provided the first quantitative study of the complex equilibria represented by equations 3 and 4. Their experiments were carried out at 1620° C., and their conclusion was that at equilibrium the product of carbon times iron oxide in the metal is approximately 0.011. Their gas compositions were not known with sufficient accuracy to determine the ratio of carbon dioxide to carbon monoxide as a function of the iron oxide content of the metal.

The effect of iron oxide content upon the ratio of steam to hydrogen in the equilibrium gas was studied by Chipman<sup>4</sup> and later by Fontana and Chipman<sup>5</sup>, who obtained an accurate value for the equilibrium constant of reaction 1 at 1600° C. More recently, Vacher<sup>6</sup>, using an improved technique, has obtained very accurate values for the several equilibrium constants involved in the evolution of carbon monoxide and carbon dioxide from liquid iron at 1580° C. In the same paper he reports approximate values for the steam-hydrogen equilibrium, which are essentially in agreement with those of the writers. The situation regarding these reactions may be summed up by stating that at the present time we know quite accurately the condition of equilibrium in the steam-hydrogen reaction (1) at 1600° and in the CO-CO<sub>2</sub> reactions (2, 3 and 4), at 1580° C. The effects of temperature upon these reactions have not previously been studied with accuracy. The determination of the effect of temperature upon reaction 1 was the object of the experimental work reported in this paper. It will also be shown how, with the aid of the data obtained and of Vacher's results at a single temperature, the effect of temperature upon the other three reactions can be computed with considerable accuracy.

#### EXPERIMENTAL METHOD

The apparatus employed in this study was essentially the same as that previously used by Fontana in his work at 1600°. The induction furnace is shown in Fig. 1. A mixture of steam and hydrogen prepared by passing purified hydrogen through a water saturator maintained at constant

temperature in a thermostat was passed into the apparatus through the sillimanite tube directed toward the surface of the melt. The gas mixture was preheated by means of a small resistance element made of platinum wire. Temperatures were measured by means of an optical pyrometer of the disappearing-filament type, which was frequently checked against the melting point of electrolytic iron,  $1530^{\circ}\text{C}$ .

Two methods were used for preparing the electrolytic iron for the experiment. In one of these the iron was melted in vacuo and allowed to solidify in the same crucible in which it was later to be used. For other experiments the iron was melted in an open magnesia crucible and cast into long rods, which could be cut up into pieces of appropriate size for melting in the small equilibrium furnace. The first method produced iron of somewhat lower oxygen content than that obtained during the equilibrium measurements, while the second method produced an iron of considerably higher oxygen content. By using these two types of iron, we were assured of approaching the condition of equilibrium from both sides.

The crucibles were made of magnesia, with the exception of the one used in run No. 5 (Table 1) which was of beryllia. The only difference noted was that in beryllia crucibles it was very difficult to obtain the high temperatures desired, probably because of the higher thermal conductivity of this material.

The liquid iron bath was exposed to the steam-hydrogen mixture for 2 hr., after which it was cooled, sectioned

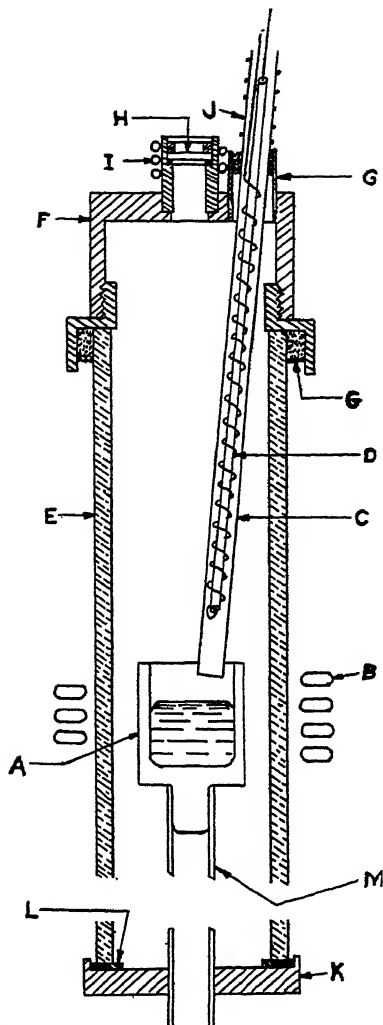


FIG. 1.—FURNACE USED IN EQUILIBRIUM STUDIES.

- A, crucible containing melt.
- B, induction coil, 20 turns.
- C, gas-inlet tube (sillimanite).
- D, platinum coil on porcelain tube.
- E, silica tube 10 in. long, 2 in. outside diameter.
- F, brass head.
- G, zinc cement.
- H, sight glass.
- I, cooling coil.
- J, chromel heating coil.
- K, brass base.
- L, asbestos washer.
- M, porcelain support.



vertically into a number of pieces, and analyzed for oxygen in the vacuum fusion apparatus<sup>7</sup>. The temperature recorded for the run is the average temperature during the last half hour. Other details of the experimental method were the same as previously reported, and need not be elaborated upon at this point.

### EXPERIMENTAL RESULTS

The results of all experiments are summarized in Table 1. The second column of the table gives the pretreatment of the electrolytic iron before the experiment. The third column contains the ratio of steam to hydrogen computed from the barometric pressure and the vapor pressure of steam at the saturator temperature, and corrected for the deviation of steam from the ideal gas law. The oxygen content of the metal is shown as the average of two or three check determinations of each ingot. The last column gives the equilibrium constant for the reaction, oxygen content being expressed as percentage of FeO.

TABLE 1.—*Experimental Results on Reaction of Steam with Liquid Iron*

Run	Iron	(H <sub>2</sub> O)/(H <sub>2</sub> )	Temperature, Deg. C.	Oxygen Analysis, Per Cent			Oxygen in Metal, Per Cent	$\frac{(\text{H}_2\text{O})}{(\text{H}_2)(\% \text{ FeO})}$
1	Vac. melt	0.337	1703	0.153	0.157		0.155	0.485
2	Vac. melt	0.165	1698	0.081	0.076		0.079	0.466
3	Vac. melt	0.319	1750	0.203	0.203		0.203	0.350
4	Vac. melt	0.215	1696	0.099	0.087	0.102	0.100	0.478
5	Vac. melt	0.168	1625	0.051	0.051		0.051	0.734
6	Vac. melt	0.165	1713	0.086	0.085		0.085	0.431
7	Vac. melt	0.129	1700	0.066			0.066	0.435
8	Vac. melt	0.125	1700	0.060	0.059		0.060	0.464
9	Vac. melt	0.180	1669	0.071	0.071		0.071	0.565
10	Open melt	0.315	1665	0.110	0.110		0.110	0.638
11	Open melt	0.296	1767	0.208	0.207	0.209	0.208	0.316
12	Open melt	0.278	1723	0.160	0.144		0.152	0.408
13	Open melt	0.257	1687	0.110	0.113		0.112	0.510
14	Open melt	0.222	1705	0.107	0.107		0.107	0.462
15	Open melt	0.247	1768	0.174	0.176		0.175	0.315
16	Open melt	0.240	1705	0.118	0.121		0.120	0.445
17	Open melt	0.230	1687	0.107	0.110		0.108	0.474
18	Open melt	0.220	1705	0.125	0.107	0.107	0.107	0.457
19	Open melt	0.231	1700	0.112	0.099	0.108	0.110	0.468

Nine of the experiments listed in Table 1 were carried out at a temperature of 1700° C. ( $\pm 5^\circ$ ). The relationship at constant temperature, between oxygen content of the bath and the ratio of steam to hydrogen in the gas, is shown clearly in Fig. 2. The direct proportionality indicated by the straight line is a confirmation of the results previously reported

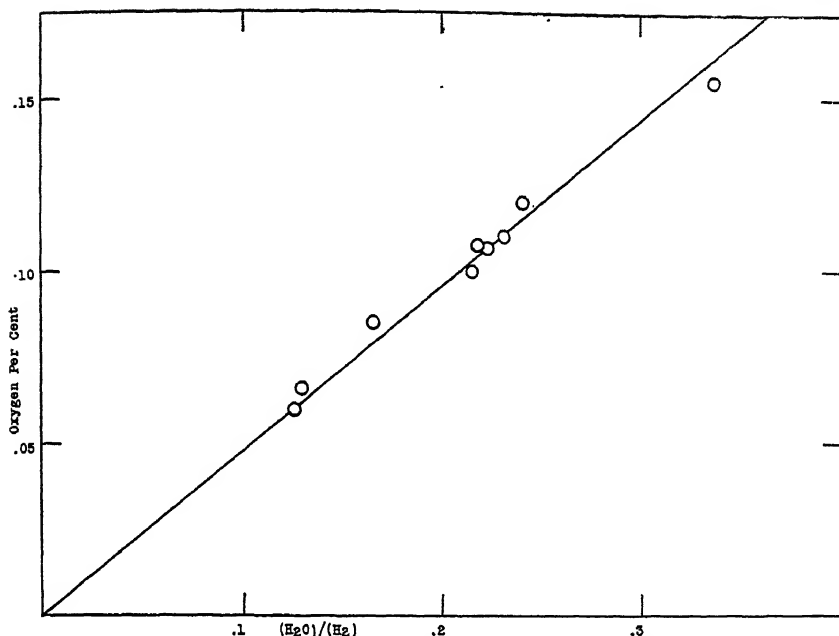


FIG. 2.—OXYGEN IN METAL AS FUNCTION OF STEAM-HYDROGEN RATIO AT 1695 TO 1705° C.

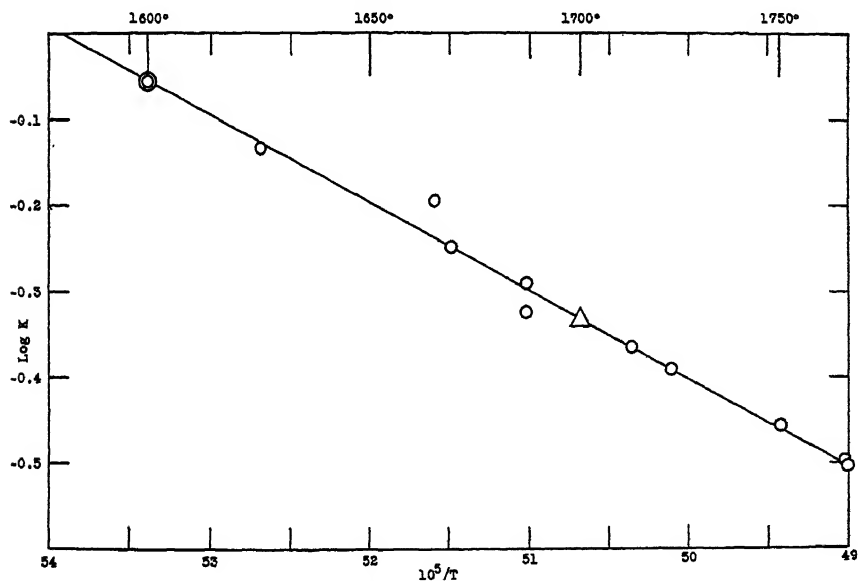


FIG. 3.—EFFECT OF TEMPERATURE UPON EQUILIBRIUM  
 $\text{FeO (IN Fe)} + \text{H}_2 = \text{Fe(LIQ.)} + \text{H}_2\text{O}$ .

Logarithm of equilibrium constant is plotted against reciprocal of absolute temperature. Triangle, average of nine determinations at 1700° C. Double circle, average of Fontana's results at 1600° C.

at 1600°. The equilibrium constant of the reaction is determined by the slope of the line and may be expressed in either of the following ways:

$$K' = \frac{(\text{H}_2\text{O})}{(\text{H}_2)(\% \text{O})} = 2.09; \quad \text{or} \quad K = \frac{(\text{H}_2\text{O})}{(\text{H}_2) \times (\% \text{FeO})} = 0.466$$

The effect of temperature upon the equilibrium is most accurately represented by plotting the logarithm of the equilibrium constant against the reciprocal of the absolute temperature. Such a plot is shown in Fig. 3, which includes all of the data of Table 1 and also Fontana's final value for the same constant at 1600°. The straight line may be represented by the expression:

$$\text{Log } K = 10,200/T - 5.50 \quad [5]$$

This expression, which is based upon results in the range 1600° to 1770° C., may be extrapolated over a much wider range without much uncertainty. Table 2 shows the value of the steam-hydrogen ratio as a function of temperature and iron oxide content of the metal as computed from equation 5.

TABLE 2.—*Values of Steam-hydrogen Ratio over Liquid Iron*

FeO, Per Cent	Temperatures						
	1500° C.	1550° C.	1600° C.	1650° C.	1700° C.	1750° C.	1800° C.
0.01	0.0180	0.0124	0.0088	0.0064	0.0047	0.0035	0.0026
0.02	0.0360	0.0248	0.0176	0.0128	0.0093	0.0070	0.0052
0.05	0.090	0.062	0.044	0.032	0.0233	0.0174	0.0130
0.10	0.180	0.124	0.088	0.064	0.0466	0.035	0.026
0.20	0.360	0.248	0.176	0.128	0.0932	0.070	0.052
0.50	0.90	0.62	0.44	0.32	0.233	0.174	0.130
1.00	1.80	1.24	0.88	0.64	0.466	0.348	0.262

#### THERMODYNAMIC PROPERTIES OF GASES

Before we can proceed with the thermodynamic treatment of our experimental data and the calculation from them of some of the more important equilibria in liquid iron, it is necessary to know something regarding the properties and reactions of the gases themselves. Perhaps also at this point a brief review of the simple thermodynamic methods that will be employed is in order. In any chemical reaction there is a change in energy, and that part of the total energy change available as a driving force in the reaction is called the "change in free energy" and is denoted by the symbol  $\Delta F$ . When each reactant and each product of the reaction occurs in a chosen standard state, as for example in reaction 1, when each gas is at a pressure of one atmosphere and the concentration of FeO is 1 per cent, the change in free energy is called " $\Delta F$  standard" and is represented  $\Delta F^\circ$ . This quantity is directly related to the equilibrium

constant of the reaction at any temperature  $T$  on the absolute scale, by the useful equation,

$$\Delta F^\circ = -4.575T \log K \quad [6]$$

so that when the  $K$  of a reaction is known, its  $\Delta F^\circ$  is easily computed, and vice-versa, as will be illustrated in the following pages.

The only other equation we will need is that relating the change in free energy to the temperature,

$$\Delta F^\circ = \Delta H - T\Delta S \quad [7]$$

in which  $\Delta H$  is the heat absorbed in the reaction,  $T$  the absolute temperature, and  $\Delta S$  the increase in entropy in the reaction. For present purposes the term,  $-\Delta S$ , may be regarded merely as the temperature coefficient of the free energy. At high temperatures neither  $\Delta H$  nor  $\Delta S$  changes very rapidly with temperature, and, therefore, over a limited temperature range, say  $1400^\circ$  to  $1800^\circ$  C., the equation may be used by simply substituting the numerical values of these functions at  $1600^\circ$ .

The thermodynamic functions  $F$ ,  $H$  and  $S$  for the common gases are now known with a very high degree of precision as a result of the brilliant work of a number of investigators on the interpretation of the spectra of gaseous molecules. The data presented in Table 3 are interpolated to a standard temperature of  $1600^\circ$  C. ( $1873^\circ$  K.) from the tables of data of the following investigators: hydrogen, Giauque<sup>8</sup>; oxygen, Johnston and Walker<sup>9</sup>; steam, Gordon<sup>10</sup>; carbon monoxide, Clayton and Giauque<sup>11</sup>; carbon dioxide, Kassel<sup>12</sup>. Graphite is included in the present tabulation, although its properties are obtained from thermal rather than spectroscopic data. Gordon<sup>10</sup> suggested that the tabulations of Clayton and Giauque be increased by 0.5 entropy unit to bring them into agreement with equilibrium data. The agreement is better when a correction of 0.60 unit is applied, and this has been done in Table 3. Although the values for graphite are considerably less accurate than those for the gases, the accuracy is amply sufficient for the purposes for which the data will be used in this paper.

Since two of the quantities mentioned determine the third, it is sufficient to record any two of them. The value given in Table 3 for free energy is the difference between the free energy  $F^\circ$  at the given temperature and the total energy at absolute zero,  $E_0^\circ$ . Values of the two functions at

TABLE 3.—*Free Energy and Entropy of Gases and Carbon*

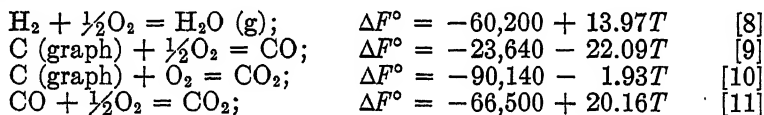
	$T$	$H_2$	$O_2$	$H_2O$	$C$	$CO$	$CO_2$
$-(F^\circ - E_0^\circ)/T$ .....	298	24.44	42.08	37.18	1.15	40.36	43.57
$S^\circ$ .....	298	31.23	49.02	45.10	1.99	47.32	51.08
$-(F^\circ - E_0^\circ)/T$ .....	1873	37.21	55.60	52.69	5.71	53.59	61.09
$S^\circ$ .....	1873	44.49	63.64	62.34	7.44	61.35	73.01

25° C. (298.1° K.) are included. In order to use these data in calculating the condition of equilibrium in any reaction involving the given substances, it is not necessary to know values of  $E_0^\circ$  for each substance, but only the increase in this quantity,  $\Delta E_0^\circ$ , which accompanies each of the three reactions by which the three compounds are formed from their respective elements. This information is obtained from the heats of formation of compounds which in turn come from the heats of combustion of hydrogen, carbon monoxide, and graphite, measured by Rossini<sup>13</sup> and by Roth<sup>14</sup>. The data are given in Table 4, in which are also included the changes accompanying the same reactions at 1600° C.

TABLE 4.—*Fundamental Gaseous Reactions*

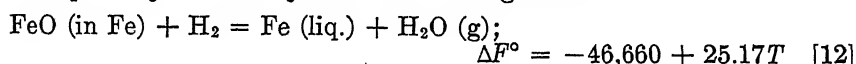
Reaction	$\Delta H_{298}$	$\Delta E_0^\circ$	$\Delta F_{1873}^\circ$	$\Delta H_{1873}$	$\Delta S_{1873}^\circ$
$\text{H}_2 + \frac{1}{2}\text{O}_2 = \text{H}_2\text{O (g)} \dots\dots$	-57,809	-57,111	-34,034	-60,200	-13.97
$\text{C (graph)} + \frac{1}{2}\text{O}_2 = \text{CO} \dots\dots$	-26,617	-27,405	-65,015	-23,640	+22.09
$\text{C (graph)} + \text{O}_2 = \text{CO}_2 \dots\dots$	-94,240	-94,162	-93,750	-90,140	+ 1.93

From these data are obtained the following equations, which may be employed without significant error throughout the range of 1500° to 2200° K.



#### FREE ENERGY OF FERROUS OXIDE

The change in free energy in the reaction of hydrogen with ferrous oxide in liquid iron is obtained from the experimental results presented in this paper. These results are represented by equation 5, which, when multiplied by  $-4.575T$  yields the following result:



and when this is combined with equation 8, the result gives the free energy of formation of ferrous oxide in a one per cent solution in liquid



iron. The free energy of liquid FeO is obtained by combining equation 13 with another equation which is based upon all of the published data on the solubility of FeO in liquid iron,

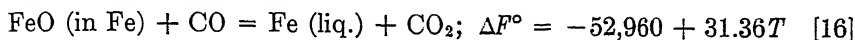


The combination of 13 and 14 yields an expression for liquid FeO, which may be used also as an approximation for the partial molal free energy of FeO in basic slags:



## REACTION OF CARBON MONOXIDE WITH FERROUS OXIDE

Our experimental data and the free-energy equations enable us to compute the ratio of  $\text{CO}_2$  to  $\text{CO}$  in the gases in equilibrium with liquid iron of any oxygen content and at any temperature. The first step is to combine equations 11 and 13 to obtain:



The equilibrium constant is  $(\text{CO}_2)/(\text{CO})(\% \text{ FeO})$  and it changes with temperature according to the expression,

$$\text{Log } K = 11,576/T - 6.855 \quad [17]$$

This is one of the three reactions studied by Vacher<sup>6</sup> and a comparison of the calculated and observed constants will be interesting. His data on six experiments that he considered most reliable are quoted in Table 5. The sixth column of this table contains his values of the equilibrium constant of equation 16. Vacher stated that his ingot 11 had not reached equilibrium with respect to its oxygen content, therefore he omitted it from the average of the carbon-oxygen product. His reasoning on this point seems to be quite sound and accordingly the results on ingot 11 are omitted from the averages of Table 5 wherever  $\text{FeO}$  is involved. They are, however, included in the average of the last column of the table, in which only the carbon content of the metal is involved. The average value of the constant of equation 16 is 0.233. Solution of equation 17 for the same temperature,  $1580^\circ \text{C.}$ , gives  $K = 0.245$ . The two sets of data are in virtually exact agreement, since the small discrepancy is within the experimental accuracy of either observer, and would be fully accounted for by a difference of only  $5^\circ$  in the temperature scales employed in the two laboratories.

TABLE 5.—Vacher's Data on the System Liquid Iron-carbon Oxides at  $1580^\circ \text{C.}$

No.	$\text{CO}_2$ in Gas, Per Cent	Carbon, Per Cent	Oxygen, Per Cent	$\frac{(\text{C})(\% \text{ FeO})}{(\text{CO})}$	$\frac{\text{CO}_2}{(\text{CO})(\% \text{ FeO})}$	$\frac{(\text{CO})^2}{(\text{CO}_2)(\% \text{ C})}$
6	10.3	0.020	0.107	0.0107	0.236	390
7	12.1	0.017	0.125	0.0109	0.245	376
8	14.3		0.168		0.222	
9	16.7		0.174		0.256	
10	11.3	0.019	0.138	0.0133	0.205	376
11	11.2	0.019	0.155	*0.0149	*0.181	370
Average (omitting values marked *)....				0.0116	0.233	378

The equilibrium ratio of  $\text{CO}_2$  to  $\text{CO}$  at various temperatures and over a wide range of oxygen content is shown in Table 6. The extension of the table to cover this wide range of temperature and oxygen content is

fully warranted by the accuracy with which the effect of temperature upon the steam-hydrogen reaction has been determined, and by the precision of the spectroscopic values of the free energies of the gases.

TABLE 6.—*Values of CO<sub>2</sub>/CO Ratio over Liquid Iron*

FeO, Per Cent	1500° C.	1550° C.	1600° C.	1650° C.	1700° C.	1750° C.	1800° C.
0.01	0.0047	0.0031	0.0021	0.0015	0.0010	0.0007	0.0005
0.02	0.0094	0.0062	0.0048	0.0029	0.0021	0.0015	0.0011
0.05	0.0235	0.0156	0.0105	0.0073	0.0051	0.0037	0.0026
0.10	0.0470	0.0312	0.0210	0.0146	0.0103	0.0074	0.0053
0.20	0.0940	0.0624	0.0420	0.0292	0.0206	0.0148	0.0106
0.50	0.235	0.156	0.105	0.073	0.0515	0.037	0.0265
1.00	0.470	0.312	0.210	0.146	0.103	0.074	0.053

## CARBON IN LIQUID IRON

Equilibrium in the reaction of the gases with carbon in liquid iron may be represented by equation 18, the constant of which is recorded in the last column of Table 5. The average value of  $K$  at 1580° C. is 378,



and the free energy change is  $-4.575 \times 1853 \log 378 = -21,850$  cal. At other temperatures precise information is lacking, but an approximate equation may be obtained in the following way.

The analogous reaction in which the carbon is dissolved in austenite has been studied by several experimenters, and their data were used by one of the writers<sup>15</sup> as a basis for computing the equilibrium involving carbon in liquid steel. The extrapolation yielded a value of  $\Delta F^\circ = 40,080 - 34.45T$  for the free energy change in reaction 18. Now this extrapolation neglected, because it was unknown, the thermal effect of transferring iron carbide from austenite to liquid iron, and it would not be surprising to find that the heat term of the equation is in error. An empirical correction of 1900 cal. applied to this term brings the old expression into exact agreement with Vacher's data, and the result is:



The composition, with respect to its CO and CO<sub>2</sub> content, of any gas in equilibrium with liquid steel of any carbon content, below about 0.20 per cent, and within a considerable range of temperature and pressure, may be computed from equation 19. For the special case of one atmosphere total pressure of CO plus CO<sub>2</sub>, the carbon dioxide content of the gas in equilibrium with liquid steel of specified carbon content is shown in Table 7. The table also contains the values of the equilibrium constants by means of which the gas compositions under other conditions may be obtained. In general, the gas tends to become more nearly pure

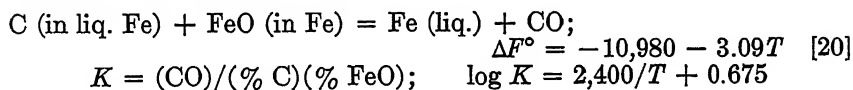
carbon monoxide at higher carbon content, higher temperature and lower pressure.

TABLE 7.—*Carbon Dioxide in Gases over Liquid Steel*  
(Remainder of gas is CO. Total pressure, 1 atmosphere)

Temperature	1500° C.	1550° C.	1600° C.	1650° C.	1700° C.
<i>K</i>	226	314	430	580	760
Carbon, Per Cent	Carbon Dioxide in Equilibrium Gas, Per Cent				
0.01	25.0	20.2	16.3	13.0	10.5
0.02	15.7	12.2	8.4	7.4	5.8
0.03	11.5	8.8	6.7	5.2	4.0
0.04	9.1	6.9	5.2	4.0	3.1
0.05	7.6	5.7	4.3	3.2	2.5
0.06	6.1	4.8	3.6	2.7	2.1
0.08	5.0	3.7	2.8	2.1	1.6
0.10	4.1	3.0	2.2	1.7	1.3
0.12	3.4	2.5	1.9	1.4	1.1
0.15	2.8	2.0	1.5	1.1	0.9
0.20	2.1	1.6	1.1	0.8	0.6

#### *Carbon-iron Oxide Reaction*

It has been pointed out that the product of percentage of carbon by percentage of iron oxide in liquid steel approaches a nearly constant value. This product may now be calculated at any temperature within the usual steelmaking range. When equations 16 and 19 are added together the expression of equation 20 results.



This constant has played an important part in previous studies of steel-making reactions. It is generally written as the reciprocal of the above constant and given the special designation *m*. We may, therefore, write,

$$m = (\% \text{ C})(\% \text{ FeO})/(\text{CO}); \quad \log m = -2,400/T - 0.675 \quad [21]$$

Values of the equilibrium constant at several temperatures are given in Table 8. The equilibrium product of carbon by iron oxide is equal to *m* only when the pressure of carbon monoxide is one atmosphere. Where the total pressure is one atmosphere and the only gases present are CO and CO<sub>2</sub>, the percentage of each may be obtained from Table 7. This is used in computing the carbon-iron oxide product shown in Table 8. The tabulation ends at 0.20 per cent carbon, and it would be unwise to carry the calculations beyond this point without more experimental data.



TABLE 8.—*Carbon-Iron Oxide Reaction*

Temperature	1500° C.	1550° C.	1600° C.	1650° C.	1700° C.
<i>m</i>	0.0094	0.0102	0.0111	0.0120	0.0129
Carbon, Per Cent	Values of Product Per Cent C by Per Cent FeO at One Atmosphere Pressure				
0.01	0.0070	0.0081	0.0093	0.0105	0.0116
0.02	0.0080	0.0090	0.0102	0.0111	0.0121
0.05	0.0087	0.0096	0.0106	0.0116	0.0126
0.10	0.0090	0.0099	0.0108	0.0118	0.0127
0.20	0.0092	0.0101	0.0110	0.0119	0.0128

## EVOLUTION OF GASES FROM RIMMING INGOTS

In applying the foregoing data to a study of gases evolved from steel ingots, it is necessary to remember that the composition of the metal from which the gases are liberated is neither that of the ladle sample nor of the solidified ingot. The segregation that occurs during the freezing of the ingot is due in large measure to the fact that all impurities are more soluble in the liquid than in the solid metal. Every dissolved substance, therefore, tends to become more concentrated in the liquid metal as the more nearly pure solid metal is formed. The rejection of impurities from the solidifying metal doubtless establishes a film or layer of liquid metal at the interface, within which the concentration of dissolved substances is greater than in the bulk of the liquid metal. It is probably within this film that the gases are liberated. The evolved gases, consisting mainly of the oxides of carbon, carry off enough of these elements to affect appreciably the composition of the remaining liquid. The actual composition of the liquid metal at the source of the evolved gases is at any moment during the solidification a resultant of these two processes of segregation and gas evolution. Without more data than are available at the present time, it is difficult to predict what this composition might be.

Part of the evolved gas is nitrogen and a simple computation will show at least the order of magnitude of its occurrence. The solubility of nitrogen in liquid iron at the melting point is 0.039 per cent<sup>18</sup> and it is usually found to an extent of about 0.004 per cent in open-hearth steel. Since its concentration is proportional to the square root of its pressure, by Sieverts' Law, and its concentration is about one-tenth of the atmospheric saturation value, its pressure should be about one-hundredth of an atmosphere. Allowing for some segregation in the liquid film at the interface, its pressure may be as high as two or three-hundredths of an atmosphere, so that in the gases evolved from such a steel the nitrogen content should be between 1 and 3 per cent. For a Bessemer steel containing 0.015 per

cent nitrogen, the gases might be expected to contain 15 to 20 per cent of this element.

A similar estimate may be made for hydrogen on the basis of Sieverts'<sup>17</sup> solubility determination of 0.0021 per cent in the liquid at the melting point. A heat containing 0.0003 per cent hydrogen should possess a hydrogen pressure proportional to the square root of its concentration, or about  $\frac{1}{49}$  atmosphere. The hydrogen content of the gases evolved from such a heat would be about 2 per cent, or, allowing for some concentration in the interfacial film, perhaps as high as 3 to 5 per cent.

The gases evolved from a normal rimming ingot of open-hearth steel might reasonably be expected, on the basis of these estimates, to contain from 1 to 3 per cent nitrogen and from 1 to 5 per cent hydrogen. The balance of 92 to 98 per cent will consist of carbon monoxide and carbon dioxide. Its distribution between these two oxides will in general depend upon the carbon and iron oxide content and the temperature of the active film of liquid metal adjacent to the solidified shell of the ingot. As a first approximation, the data of Tables 6 and 7 at 1500° might be applied. According to the latter, liquid steel of 0.08 per cent carbon would be in equilibrium with gas containing 5 per cent CO<sub>2</sub> and 95 per cent CO. Remembering that the sum of these gases is less than 100 per cent, and that the carbon content of the active film is probably greater than the ladle analysis, it is seen that the carbon dioxide content of the gases evolved from a steel of 0.08 per cent carbon ladle analysis is in all probability less than 5 per cent.

It is not the purpose of this paper to attempt an accurate prediction of the composition of gases evolved from rimming ingots, nor indeed to discuss that subject at any great length. Rather, it is our purpose to present the equilibrium data, to call attention to the fact that ingot solidification is not an equilibrium process, and to point out the need for detailed information on the mechanism of ingot solidification, without which the thermodynamic data cannot accurately be applied to the problem. Once the mechanism is fully established, thermodynamic calculation can be depended upon to establish the limits within which the mechanism must operate.

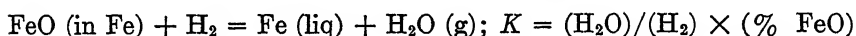
As a step toward working out such a mechanism, it is postulated that an active film exists within the liquid metal adjacent to the solidified wall of the ingot, that the film contains a greater proportion of dissolved substances than does the bulk of the liquid metal, and that it is the seat of formation of gas bubbles. The relationship of the composition of the film to that of the main body of liquid metal and to the rate of solidification remain to be worked out. The temperature of the film and the rate of cooling of the liquid metal ought to be determined experimentally. Changes in composition of the liquid metal during solidification should be studied experimentally and correlated with studies of segregation in the

ingot. When these data are available, and when the actual compositions of the evolved gases have been reliably established, it ought to be possible with the aid of the data presented in this paper to compute the limits within which the composition of the active film must lie.

### SUMMARY

Previous work has established the condition of equilibrium in the reactions of liquid iron with steam at 1600° and with the oxides of carbon at 1580° C. The present work was undertaken for the purpose of extending our knowledge of both systems over the entire range of steelmaking temperatures.

An experimental study has been made, covering the range 1600° to 1770° C., of the equilibrium constant of the reaction:

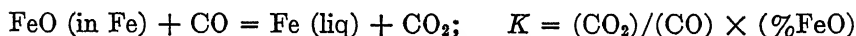


At 1700° the oxygen content of the metal is proportional to the steam-hydrogen ratio in the gas, confirming results of previous investigations. The equilibrium constant is, therefore, independent of the iron oxide content and a function of temperature only. The experimental data are represented by the equation:

$$\text{Log } K = 10,200/T - 5.50$$

In order to apply the experimental results to reactions involving other gases, a compilation has been made of the thermodynamic properties of gases at 1600° C. as obtained by modern spectroscopic methods. Equations are derived for the change in free energy accompanying reactions among the several gases, including their reactions with carbon.

The calculated equilibrium constant of the reaction,



is in virtually exact agreement with Vacher's experimental determinations, which may now be extended by calculation, to cover a wide range of temperature.

Tables are given to show the effect of iron oxide and carbon in the liquid metal on the composition of the equilibrium gas at several temperatures.

The constant for the reaction of carbon with FeO in liquid steel is computed for several temperatures, and a table is presented showing the product of percentage C by percentage FeO at atmospheric pressure, and over a wide temperature range, as a function of carbon content.

The evolution of gases from rimming ingots is discussed, and it is pointed out that until the mechanism of gas evolution is more fully understood an exact thermodynamic treatment of the problem is impossible. Some features of a probable mechanism are suggested, including the

postulate that the gases are evolved from an active film of liquid metal adjacent to the solid-liquid interface. A rough estimate of the composition of gas evolved from a low-carbon rimming ingot is made.

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## DISCUSSION

(L. F. Reinartz presiding)

C. H. HERTY, JR.,\* Bethlehem, Pa.—In the work we have been doing on gas evolution, we find that the composition of the gases, when we are sure that everything is right with the experimental work, is very close to Dr. Chipman's general prediction, and there does not seem to be any question about the correctness of his prediction. Under ideal conditions of experimentation, we seldom find as high as one per cent nitrogen, and in order to have the concentration he mentions in the gas, it must be assumed that the hydrogen and nitrogen are in solution and not in combination in the metal.

H. C. VACHER,† Washington, D. C. (written discussion).—It is evident from the paper by Dr. Chipman and Mr. Samarin that the free energy of ferrous oxide in liquid iron rests on a firm experimental foundation. The free energy has been determined over a range of temperature, 1500° to 1800° C., and the activity has been shown to be proportional to the oxygen content. However, the same cannot be said about the reaction  $C \text{ (in liquid Fe)} + CO_2 = 2CO$ . The activity of carbon has not been determined over a range of carbon content, nor has the equilibrium content been determined over a range of temperatures. The experimental research worker does not seem to be attracted to this reaction. Is this because of experimental difficulties or lack of importance?

The experimental difficulties, when the work is attempted at one atmosphere pressure, is nicely summarized in Table 7. However, these difficulties would be lessened if it were possible to conduct the experiments at 10 atmospheres pressure. Table 9 shows the percentage of carbon dioxide, at 10 atmospheres, in equilibrium

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with the systems liquid iron-austenite and liquid iron-graphite at 1200°, 1300°, 1400° and 1500° C. The values were obtained by using equation 19. The carbon values were obtained from the iron-carbon equilibrium diagram (*Metal Progress*, November 1936,

TABLE 9.—*Equilibrium Expected at Ten Atmospheres*

Temperature, Deg. C.	$K_{19}$	Liquid Iron-austenite		Liquid Iron-graphite	
		C, Per Cent	CO <sub>2</sub> , Per Cent	C, Per Cent	CO <sub>2</sub> , Per Cent
1200	20.0	3.7	11	4.3	9
1300	49.6	2.8	6.5	4.6	4
1400	111	1.8	4.5	4.8	2
1500	226	0.08	28.5	5.0	1

page 49). This table shows that it should be possible to determine the activity of carbon in liquid iron over a considerable range of carbon content and the equilibrium constant over a range of temperature, providing, of course, a furnace could be designed to operate at 10 atmospheres pressure.

A. B. KINZEL,\* New York, N. Y.—The confirmation of the equilibrium constant value of 0.01 as a satisfactory working constant is interesting. This value has now been checked by many laboratory experimenters as well as by melting experience, and would seem to be well founded. It does imply the presence of carbon dioxide as well as carbon monoxide in the reaction. It is interesting to note that both in Vacher's special experiments and in our own the elimination or reduction to negligible quantities of carbon dioxide reduces the apparent equilibrium constant to a much lower order of magnitude.

J. CHIPMAN.—Mr. Vacher's suggested experiments on the iron-carbon-oxygen system at 10 atmospheres would certainly yield valuable data. His table showing the expected equilibrium conditions at high pressure is based upon an extrapolation of equation 19 to much higher carbon contents than it was intended to apply to, therefore the table cannot be expected to be numerically correct.

The reason this reaction with carbon has not been studied, I think, is because Mr. Vacher made an admirable study of it at one temperature and at low-carbon contents, and the rest of the world had been hoping he would pursue it to other temperatures and higher percentages of carbon. We are hoping some day he will get back to that because the work offered so much promise of useful information.

Dr. Herty's remark regarding the nitrogen content is very well founded. Nitrogen lower than that predicted might well be expected if any metal other than iron is present to form a more stable nitride than iron forms. Our value 0.04 for the solubility of nitrogen in liquid iron is applicable only in the absence of such elements as manganese, silicon and aluminum. Of course, we would have only manganese present in a rimming steel, but in the presence, say, of 0.40 per cent Mn, the solubility of nitrogen is probably distinctly higher than it is in pure iron, so that the gas evolved would be lower in nitrogen.

The reason that the present data are in agreement with Vacher's results, but not with those of Kinzel and Egan, is probably because the experiments of the latter did not attain or even approach a state of equilibrium. Their value for the carbon-iron oxide product was approximately one-twentieth of ours. It was not an equilibrium

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constant, and cannot be used in thermodynamic calculations. An explanation of the occurrence and apparent reproducibility of the lower value would be a useful contribution to our knowledge of the reaction.

L. S. DARKEN,\* Kearny, N. J.—We have been working on the same sort of thing as the authors, and when it has been possible to find reliable low-temperature information and good temperature coefficients we were able to reproduce some of Mr. Chipman's constants at these higher temperatures.

I should like to ask Dr. Chipman how confident he feels of the heats implied by the temperature coefficients of his equations. For example, if we subtract the equation for the reaction of graphite with  $\text{CO}_2$  to give  $2\text{CO}$  (equation 9 — equation 11) from the equation for the corresponding reaction for carbon in iron (equation 19) we get a heat of transition from graphite to carbon in iron of the order of magnitude of about 1000 cal., I believe, which does not seem reasonable. It corresponds to a heat of fusion and it seems to me that a higher value for that heat would be more reasonable. Similarly the heat of solution of  $\text{FeO}$  in  $\text{Fe}$  (26,300 cal. from equation 14) seems unreasonably high. Of course, the change in those heats would not affect the value of these constants at the temperatures at which they are measured. I was just referring to the heats derived from the equations and not the values of the constants themselves.

J. CHIPMAN.—It is pretty difficult to tell about the heat effects, because no one has measured the heat effect involved in the transition from graphite to carbon in liquid steel. It would be particularly difficult to estimate it at low carbon contents because of the unknown heat of dilution, so that there is really nothing against which one can check with regard to this heat effect. The heat term in equation 14 is based upon solubility data of Herty and of Körber and Oelsen and is as dependable as the original data.

The heat terms implied in reactions 1 and 2 are known with as good an accuracy as our temperature measurements would justify. The temperature measurements at the solidification temperature of liquid iron are probably good to five degrees or so, but at higher temperatures they depend upon the emissivity of liquid iron remaining constant up to high temperatures, and no one has measured the emissivity of liquid iron at temperatures appreciably above the melting point. If later it should be found that the emissivity of liquid iron changes at very high temperatures, a correction would have to be applied to the heat effects to take that into consideration.

When we go from equations 1 and 2 to equations 3 and 4, we are stepping across a gap in regard to the certainty of the computations. Three and four are distinctly less precise than one and two, particularly with regard to heat effects.

S. L. HORT,† Milwaukee, Wis.—The discussion this morning has related rather generally to producing blowholes, but some of us happen to be on the receiving end of these blowholes and it is important to keep up with the progress that is made even in their production. In that connection, I want to ask Dr. Chipman a question. From his discussion, I would assume that the gas evolved during the rimming action is a homogeneous gas composed approximately of the constituents given. Are we to consider that the gas that comes off is homogeneous, or do the gases come off serially and, if so, how does that affect this general picture?

J. CHIPMAN.—I do not think that there will be any possibility of hydrogen and nitrogen,  $\text{CO}$  and  $\text{CO}_2$  separating themselves from each other during the rimming action, because gases always tend to mix, and the total pressure is the sum of the pres-

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tures of all these gases, so that I see very little chance that they would come off independently, or that any one gas is responsible for the blowholes.

The gas composition might be expected to vary during the rimming period, but its variations would not be expected to be very large. Klinger found considerable variation, part of which I think is attributable to the fact that he used some sort of a sieve to collect gases, and he had a great deal of air in there. Another part is attributable to the fact that he continued to pump off the gases long after the ingot had frozen over, whereas the estimates that I have just given are in no wise intended to apply to gases that might be pumped off after the thing solidified, but only to the gases that are actively evolved from the ingot during its rimming period.

L. F. REINARTZ,\* Middletown, Ohio.—Is it not a fact that the Germans have experimental data to show that more hydrogen comes off toward the end of the rimming period than right at the start?

J. CHIPMAN.—I think they came to within 99.44 per cent before they quit, but their ingot had solidified clear across before that happened.

B. M. LARSEN,† Elizabeth, N. J.—I do not think it makes much practical difference, but is it not reasonable to assume that the carbon monoxide and carbon dioxide are primary gases and that the others diffuse into them from the liquid? With a rapid rate of reaction, that might affect the composition, because of rates of diffusion being involved.

J. CHIPMAN.—I think what you are saying is that if we have an active film at the solidifying interface, and if that film is giving more CO and CO<sub>2</sub>, in comparison with the other gases, than would correspond to equilibrium conditions, hydrogen and nitrogen will diffuse into the gas bubbles as they rise. If the total pressure is approximately one atmosphere or a little higher, and the pressure of CO + CO<sub>2</sub> is about 0.95 atmosphere, whereas nitrogen and hydrogen are about 0.02 or 0.03 atmosphere, certainly CO and CO<sub>2</sub> are primary gases. But the actual gas that forms the blowholes and the actual gas responsible for the rimming action will contain some of the other gases as long as they are present. -

G. E. DOAN,‡ Bethlehem, Pa. (written discussion).—When I see the valuable work which Dr. Chipman and his associates have done at the University of Michigan, as reported in this paper and as has been reported previously by Dr. Chipman, especially in the process of steelmaking, I am led to believe that the steel industry must often fall to wondering whether it would not in the end benefit itself more by supporting Dr. Chipman's research at the University of Michigan than by withdrawing him from the academic atmosphere into a private industrial laboratory. There is a similar example in the work Dr. Herty carried out for the Bureau of Mines at Pittsburgh, with the support of a fund raised by industry to enable him to carry out researches in the physical chemistry of steelmaking, which have led to such valuable results for the steel industry as a whole. I would not question the productivity of private industrial laboratories, for they have turned out very valuable results, but it appears probable that research of a fundamental nature is often more successful when carried out in university laboratories with industrial support than under any other circumstances.

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[The following discussion refers also to the papers that begin on pages 370, 378 and 401, respectively]

C. BENEDICKS\* AND H. LÖFQUIST,† Stockholm, Sweden (written discussion).—In the freezing of steel ingots, the main type of the ingot obtained can be said to be determined by the location of the "heat center," as earlier advanced by the present writers<sup>18</sup>. Two main types thus exist—those possessing a low heat center (Fig. 4) and those with a high heat center (Fig. 5). This consideration, although a very simple one, requires a good deal of elucidation.

The different layers formed during cooling, as schematically shown by the figures, are known to be:

1. The *chill layer*, having the same composition as the ground metal.

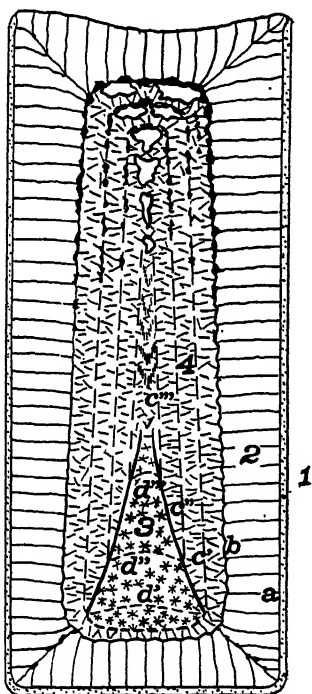


FIG. 4.

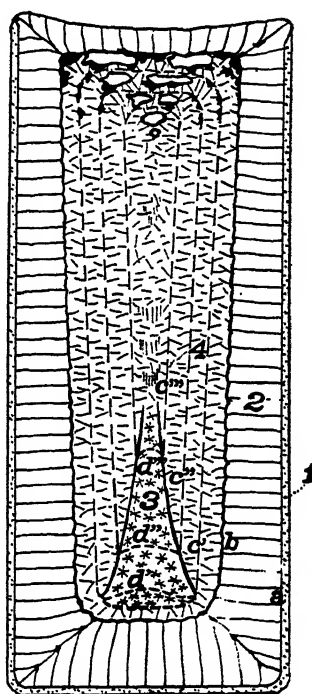


FIG. 5.

2. The *columnar zone*, consisting of columnar crystals with a relatively low content of impurities (sulphide and silicate slag). In certain kinds of steel pencil-like blow-holes occur.

3. The *sedimentary cone*; generally purer, but having a higher amount of silicate slag than the average. This denomination was introduced under the supposition that iron contracts on freezing (causing sedimentation). The correctness of this supposition was proved later on<sup>19</sup>. The sedimentation of the Fe crystals assumed to be

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† Metallurgist.

<sup>18</sup> C. Benedicks and H. Löfquist: *Nonmetallic Inclusions in Iron and Steel*, 226, London, 1930.

<sup>19</sup> C. Benedicks, N. Ericsson and G. Ericson: *Jernkontorets Ann.* (1929) 113, 423 *Archiv Eisenhüttenwesen* (1930) 3, 473.



formed primarily around minute silicate particles must occur in preference in the downward convection currents in the front of the freezing zone 2.

4. The *granular zone*, containing more or less pronounced slag streaks ("V-segregates," "ghost lines") in front of the columnar zone in the upper part of the ingot—especially formed on inward-sloping surfaces. Further, in killed steel, a pipe occurs, with coarse accumulations of sulphides as well as of silicates, surrounded by the range of "V-segregations" having high sulphide content.

The two types originally were claimed to have validity only in cases without gas evolution. The formation of gas during freezing, giving blowholes, however, does not influence the main type of ingot as far as heat center is concerned<sup>20</sup>.

The principal phenomena to be considered during freezing are the following:

1. Differential freezing, resulting in segregation in the mother liquor on crystallization, eventually with the formation of a liquid slag phase.

2. Periodicity in freezing, due sometimes merely to the liberation of the latent heat of crystallization, or to a certain interaction between differential freezing and change of temperature gradient.

3. Increase in the density of steel on solidification.

4. Convection currents in the molten steel.

5. Gas formation.

Of these phenomena, the periodicity in freezing, which at first was considered by the authors for killed steel<sup>21</sup>, has been clearly shown to be of influence also in rimming steel, appearing not only in a periodic sequence of impurities (sulphides<sup>22</sup>) but also in a periodicity of the inner blowholes. As a matter of fact, the enrichment in the mother liquor of dissolved and finally precipitated oxide and sulphide, giving a fluid oxide-sulphide slag in periodic arrangement, is accompanied by a similar enrichment of carbon, giving rise to bubbles<sup>23</sup> of CO.

Periodicity on a smaller scale has been found between the chill layer and the main columnar zone, especially at the bottom of a Parsons-Duncan ingot, and the explanation given is similar to that given by the authors<sup>24</sup>. It must be emphasized, however, that, as a general rule, crystallization is a periodic phenomenon, on account of the liberation of latent heat of solidification. Thus, a concentrated solution of sodium hyposulphite frequently is found to give a plain lamellar structure, due to this cause.

A very marked periodicity in structure in centrifugal castings<sup>25</sup> may be explained as a result of periodicity in freezing, and difference in density of solid and liquid steel, augmented by centrifugal forces. The sample consisted of a cylindrical wall with a thickness of 2.86 in. and an outer diameter of 50 in., cast in a horizontal container, rotating at a speed of 220 revolutions per minute. The carbon concentration, being as a mean 0.20 per cent, showed in a section two marked peaks, amounting to 0.32 and 0.22 per cent C, at about 0.5 and 1.5 in. below the outer surface, with only about 0.15 per cent C between and at the sides of these peaks. On cooling, the crystals of Fe first formed, having a low carbon content and a higher density than the mother liquor, apparently are thrown out during centrifuging towards the outer surface—the centrifugal forces being found by calculation to be 17 times as large as gravity. A solid outer shell low in carbon thus will be formed, and inside it a certain liquid region of a higher carbon content, and consequently with a lower freezing point, will be obtained.

<sup>20</sup> C. Benedicks: *Jnl. Iron and Steel Inst.* (1932) **125**, 153; *ibid.* (1933) **128**, 423.

<sup>21</sup> Reference of footnote 18, 231.

<sup>22</sup> First reference of footnote 20.

<sup>23</sup> C. Benedicks: *Jnl. Iron and Steel Inst.* (1933) **128**, 423.

<sup>24</sup> L. Northcott: *Jnl. Iron and Steel Inst.* (1934) **129**, 151.

<sup>25</sup> Iron and Steel Institute, Sixth Report on the Heterogeneity of Steel Ingots, 39. London, 1935.

On cooling further, crystals of iron of low carbon content will be formed in the unchanged molten steel inside the carbon-rich region, which has not yet begun to crystallize (and probably possesses a lower rotating speed). On centrifuging, the crystals are partly thrown out into the carbon-rich region, causing a certain decrease in its mean carbon content and causing its solidification. Inside the second zone of low carbon content so formed, a new region of enrichment of carbon will be obtained, although less marked than the first one. The structure found thus may be said to be in a very good agreement with what is to be expected from the theory of periodicity in freezing, here strongly augmented as to its influence by the centrifuging forces. This explanation is much simpler than the assumption that the concentration sequence might be due to some Soret effect.

It may be noted here that, as a general rule, a crystal must grow mainly in the direction of the temperature gradient, towards the hotter part, or, in other words, in a direction perpendicular to the isotherms. When crystallization sets in, the vertical wall of the mold will approximate an isotherm; therefore the crystals will grow approximately in a horizontal direction. Frequently, however, there is an upward tendency of growth, corresponding, according to the general rule mentioned, to a slightly higher temperature on the upper, growing side of an approximately horizontal crystal. The reason for such a heat distribution will be essentially that in the front of the growing columns a downward convection current will exist (in the absence of gas evolution), which must give a slight vertical temperature gradient, causing a slight upward trend of the columns.

Another point that may be discussed here is the influence of gas evolved. Through the very thorough investigations of Edwards and co-workers<sup>26</sup>, much knowledge has been gained in this field. Regarding the formation of a blowhole-free solid "rim" in rimming steel, the explanation earlier given by the authors<sup>27</sup> has been accepted and supported by later experiments<sup>28</sup>. In the explanation, mention may first be made of the method recommended by Faraday for producing a clear ice layer, free from blowholes. This method was to use a feather for wiping the frozen ice wall, so as to remove mechanically the air bubbles formed. It is quite plain that the same wiping action must be exerted by a gas stream if its velocity is sufficiently high. In steel having a sufficiently high content of gas, there will be evolved on freezing rather large quantities of gas (principally CO, formed from FeO and C in the enriched liquid). This vigorously ascending gas will remove the gas bubbles formed on the front of the growing crystals, and a blowhole-free "rim" will be formed. This consideration seems to account satisfactorily for the striking results, otherwise difficult to explain, obtained in the investigations quoted.

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<sup>26</sup> C. A. Edwards and H. N. Jones: Iron and Steel Inst., Special Report No. 4, Fifth Report on the Heterogeneity of Steel Ingots, 39. London, 1933.

<sup>27</sup> Reference of footnote 23.

<sup>28</sup> C. A. Edwards, R. Higgins, M. Alexander and D. G. Davies: Iron and Steel Inst. *Special Report* No. 9, Sixth Report on the Heterogeneity of Steel Ingots, 193. London, 1935.

## Some Factors Affecting Life of Ingot Molds

By W. J. REAGAN,\* MEMBER A.I.M.E.

(Cleveland Meeting, October, 1936)

IN a study of the life of ingot molds, it is essential to eliminate all of the variables. In the commercial manufacture of steel this is almost an impossibility. In this study many of the variables have been eliminated, and because of the unusually consistent furnace practice, with small variations in the type of steel manufactured, and a similar type of mold design for all ingot sizes, it is possible to determine with some degree of accuracy the cause of variations in ingot-mold life.

All of the ingot molds in this study were used in the production of basic open-hearth killed steel with chemical analyses within the following range: C, 0.50–0.85 per cent; Mn, 0.60–0.80; Si, 0.20–0.30; S, 0.04 max.; P, 0.04 max. All ingot molds were of the closed-bottom type and used for bottom casting only. None of the molds in the study failed from cutting of the sides due to top casting; in fact, on only rare occasions are any molds used for top casting.

The general type of this mold is shown in Fig. 1. All sizes have rather a heavy band of metal, about 6 in. wide, at the top to give mechanical strength at this point, and all have cast lugs. Cross sections of the various sizes from top and bottom sections are shown in Fig. 2. Ratios of wall thickness to ingot weight, ratio of ingot diameter to ingot length, and other figures of interest are shown in Table 1.

In the majority of cases, the cause of failure in this type of mold is due to heavy fire cracking on the "flats" at a point from 3 to 6 in. from the bottom radius of the mold. Fig. 3 pictures this type of failure. The start of failure at these points usually begins with a very small section of the interior surface becoming involved. As a rule, a section of 1 or 2 sq. in. is the first noticeable indication that mold failure is taking place. Gradually the small section increases until a sizable cavity develops, causing a protuberance on the bottom of the ingot, which eventually becomes too large to be stripped. The mold is then removed from service. At the time of failure, this cavity often reaches a size of about 5 sq. in. and about  $\frac{1}{2}$  in. deep. Sometimes cavities are found on only two or three sides and at other times all twelve sides appear to be involved.

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Careful measurements of the interior of this type of mold have shown that as the life of the mold increases the interior diameter gradually decreases. In the later stages of the life of an ordinary mold this diameter may measure as much as  $\frac{3}{8}$  in. less in diameter than when the mold was placed in service. Outside diameters appear to remain constant. Apparently the greatest amount of heat is concentrated at the point of failure, causing the metal to grow or increase in size until small pieces become dislodged. Occasionally only a single heat is obtained from a mold after failure of the metal has started, but often 20 to 30 heats are obtained before final removal of the mold from service.

#### CHEMICAL ANALYSIS AND WALL THICKNESS

In this type of mold two factors seem to have the greatest influence upon the life: (1) chemical analyses of the metal and (2) wall thickness of the mold. The following data illustrate how these factors affect mold life.

Fig. 4 shows the effect of the weight of the ingot mold upon its life. The first group of molds averaged 6100 lb. each, and gave an average life

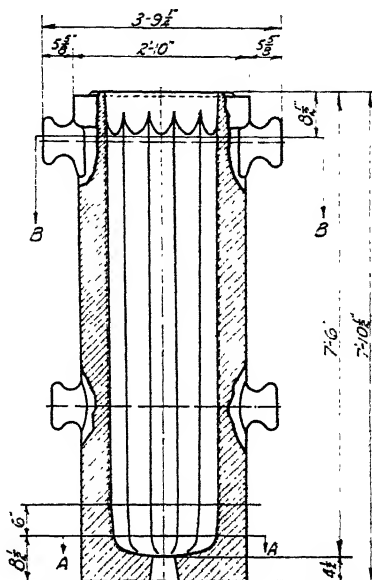
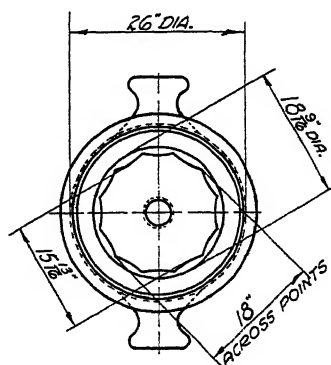
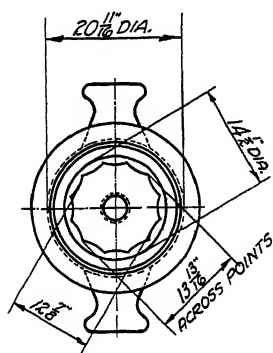


FIG. 1.—FLUTED INGOT MOLD.

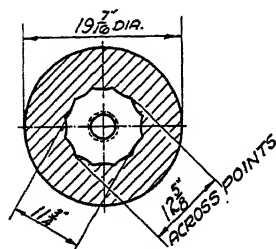


Top view of 13-inch fluted ingot mold. Top view of 17-inch fluted ingot mold  
Area at section B-B 137 square inches. Area at section B-B 235 square inches.

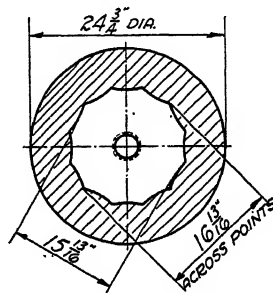
FIG. 2.—CROSS SECTIONS OF TYPE OF INGOT MOLD SHOWN IN FIG. 1.

of 194 heats or pours. In group 2 the mold weight was increased to 6900 lb. and the mold life was increased to 254 heats. For group 3

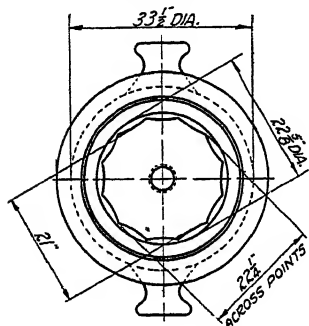
(with the same mold weight) the life was 224 heats. In group 4 the mold weight was decreased to 5300 lb. with a corresponding decrease in mold life to 163 heats. Group 5, with a mold weight similar to that of group 4, gave an average life of 154 heats. In the final mold-weight decrease



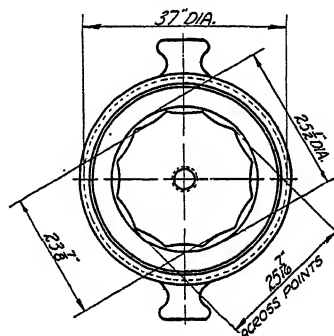
13-inch fluted mold.  
Section A-A. Area 115 square inches.



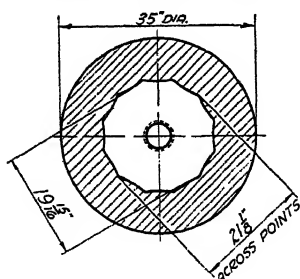
17-inch fluted mold.  
Section A-A. Area 206 square inches.



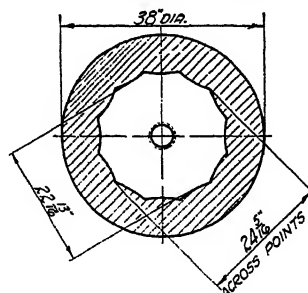
Top view of 21-inch fluted ingot mold.  
Area at section B-B 359 square inches.



Top view of 24-inch fluted ingot mold.  
Area at section B-B 465.6 square inches.



21-inch fluted mold.  
Section A-A. Area 324 square inches.



24-inch fluted mold.  
Section A-A. Area 430 square inches.

FIG. 2.—Continued.

shown in groups 4 and 5, the outside diameter of the mold was increased at the top about  $\frac{3}{4}$  in. and the bottom was decreased about  $3\frac{1}{4}$  in., to give a better weight distribution and also to give a better ratio of mold weight to ingot weight. Most of the failures in groups 4 and 5 resulted

from longitudinal cracks in the mold wall, due primarily to lack of mechanical strength and indicating that the reduction in wall thickness had been carried too far. The chemical analyses of the molds in all five groups were very similar, indicating that mold weight or wall thickness is of considerable importance in determining mold life.

TABLE 1.—*Comparative Data of Ingots and Fluted Ingot Molds*

Mold size, in. ....	13	17	18	20	21	24
Mold weight, lb. ....	5,300	10,300	10,500	13,200	15,550	17,600
Volume of iron in mold, cu. ft. wt./450	11.8	22.9	23.3	29.3	34.5	39.1
Maximum wall thickness, in.: top. ....	3.67	4.27	5.31	5.86	5.93	6.17
Bottom. ....	3.62	6.22	5.24	5.87	7.24	7.22
Average wall thickness, in. ....	3.65	5.25	5.28	5.87	6.58	6.70
Weight, lb.: ingot body only	2,950	5,165	5,865	7,880	7,930	10,320
Hot top only. ....	350	485	635	720	770	1,080
Body plus hot top. ....	3,300	5,650	6,500	8,100	8,700	11,400
Weight in hot top, per cent. ....	10.6	8.6	9.8	8.9	8.8	9.5
Taper in ingot A-A to B-B, in. per ft. . .	0.187	0.193	0.149	0.17	0.18	0.17
Ratio: Ingot length						
Ingot width (avg.) . . . . .	7.05	5.33	4.85	4.45	4.27	3.73
Mold wall area top						
Ingot area top . . . . .	1.45	1.25	1.48	1.48	1.45	1.31
Mold area bottom						
Ingot area bottom . . . . .	1.58	2.15	1.56	1.58	1.97	1.64
Avg. wall area . . . . .	1.51	1.67	1.52	1.53	1.70	1.46
Avg. ingot area . . . . .	1.51	1.67	1.52	1.53	1.70	1.46
Mold weight (body only)						
Ingot weight . . . . .	1.79	2.00	1.79	1.79	1.96	1.71
Average ingot area, in. ....	126.0	220.5	260.5	318.3	341.5	447.8
Average mold area, in. ....	190.4	369.6	396.0	486.2	580.3	656.9
Outside diameter, in.: at top. ....	20.68	26.0	29.5	32.5	35.0	37.0
Inside diameter at top, in.: flats. ....	12.87	16.94	18.31	20.18	21.0	23.88
Flutes. ....	13.81	18.0	19.44	21.37	22.25	25.43
At bottom. ....	19.43	28.75	28.31	31.50	35.00	38.00
Inside diameter at bottom, in.: flats. . .	11.75	15.81	17.26	19.15	19.94	22.81
Flutes. ....	12.62	16.81	18.39	20.34	21.13	24.31
Length ingot body, in. ....	88	88	87	88	88	8
Length hot top, in. ....	14	14	14	14	14	14

Fig. 5 graphically pictures the effect of chemical analysis upon mold life. The molds shown on groups 1 and 2 were similar, being made from the same pattern. Molds on group 3 were made from a pattern on which the outside diameter had been reduced about  $1\frac{1}{2}$  in. at the top and about  $1\frac{3}{4}$  in. at the bottom, which caused a reduction in weight of about 2200 lb. each. Owing to a change in analysis of the ingot-mold metal, the average life of the molds on group 3, instead of decreasing, increased from an average of 131 heats to an average of 178 heats. The cause is apparent. The silicon content of all three groups is substantially the

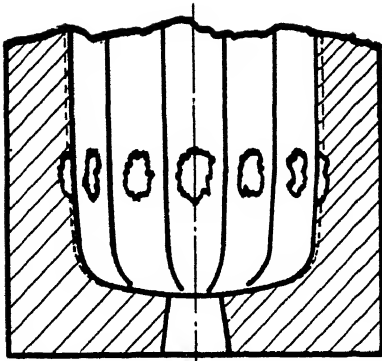


FIG. 3.—FAILURE FROM HEAVY FIRE CRACKING ON "FLATS."

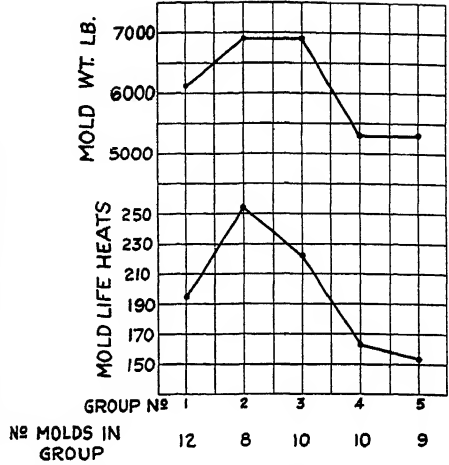


FIG. 4.—EFFECT OF WEIGHT OF 13-INCH FLUTED INGOT MOLD ON MOLD LIFE.

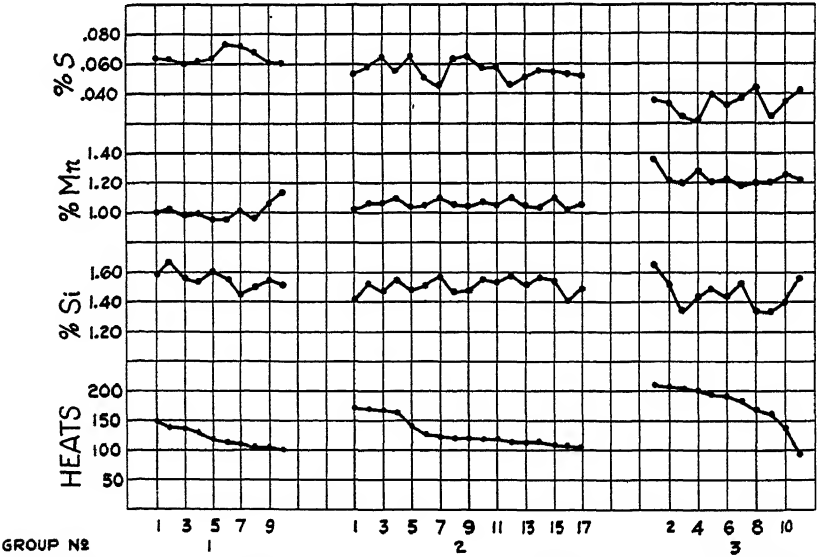


FIG. 5.—EFFECT OF CHEMICAL ANALYSIS ON LIFE OF 18-INCH FLUTED INGOT MOLD. Mold Life and Analysis

Group No.	Mold Weight, Lb.	Average Number of Heats	Average Metal Analysis, Per Cent		
			Mn	Si	S
1	13,470	121	1.01	1.55	0.064
2	13,300	131	1.06	1.51	0.056
3	11,100	178	1.23	1.46	0.034

same, but the manganese content is slightly greater in group 2 and considerably higher in group 3 than in group 1. The phosphorus content of all molds in this study are so similar that they have been neglected as

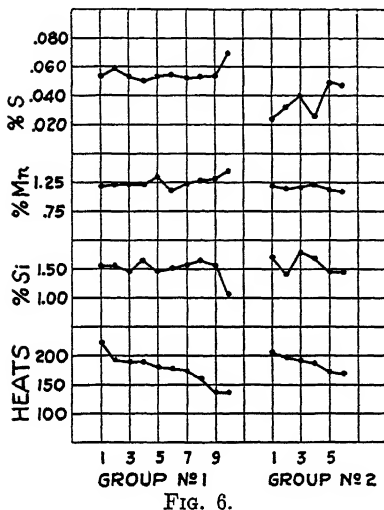


FIG. 6.

FIG. 6.—EFFECT OF SULPHUR ON LIFE OF 17-INCH FLUTED INGOT MOLD.

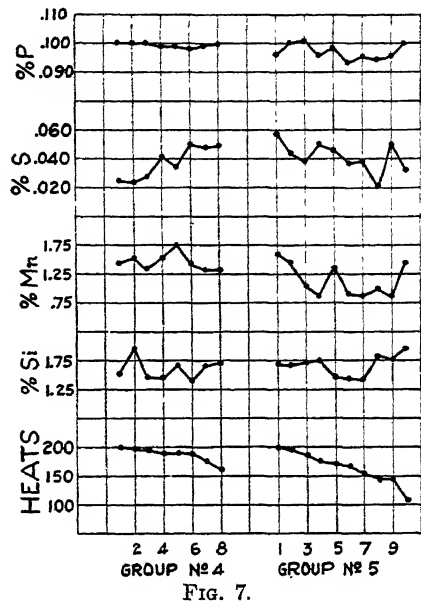


FIG. 7.

FIG. 7.—EFFECT OF MANGANESE AND POSSIBLE EFFECT OF SILICON ON LIFE OF 20-INCH FLUTED INGOT MOLD, DIRECT METAL.

*Mold Life and Analysis Groups 1, 2, 4, 5.*

Group No.	Mold Weight, Lb.	Average Number of Heats	Average Metal Analysis, Per Cent			
			Mn	Si	S	P
1	10,400	176	1.24	1.51	0.055	
2	10,400	184	1.16	1.58	0.036	
4	13,000	188	1.45	1.61	0.038	0.100
5	13,000	165	1.14	1.68	0.041	0.098

having any influence upon mold life. Most of the molds in this study contain about 0.10 per cent phosphorus.

Fig. 6 illustrates two groups of 17-in. fluted ingot molds containing sulfur. Group 2 shows a decidedly lower sulfur content than group 1, with manganese and silicon remaining about the same. This would seem to indicate that sulfur in itself has but little effect upon mold life.

Fig. 7 also illustrates the effect of manganese and the possible effect of silicon upon mold life. It has been noted in some instances that too high a percentage of silicon seems to have a detrimental effect upon mold life. The manganese content of the second group is noticeably lower and the average mold life is also lower. The last three molds shown in



group 5 all have a silicon content of over 1.75 per cent, and these three molds gave the lowest life of any in the group, in spite of the fact that one (the last in group 10) contained about 1.45 per cent manganese, which ordinarily would have insured good mold life. The value of silicon in mold life is not very clearly determined, too much silicon seeming to be as bad as too little.

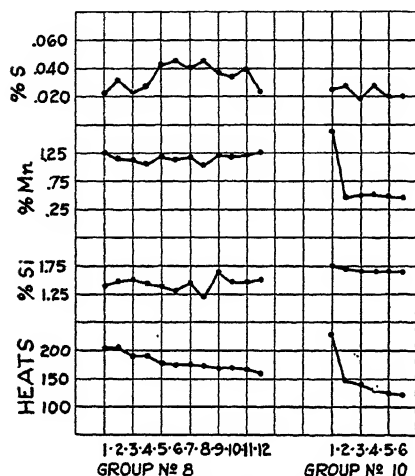


FIG. 8.—EFFECT OF MANGANESE ON LIFE OF 21-INCH FLUTED MOLD.

Group 8, mold weight, 15,300 lb.; group 10, mold weight, 15,300 lb.

Group 8, mold weight, 15,300 lb.; group 10, mold weight, 15,300 lb. The mold with the exceptionally high life is still in use and may be good for some time longer.

Fig. 9 illustrates the life of four groups of 24-in. fluted molds. In group 1 the four molds shown were all direct-metal molds. Group 2 contains all cupola-metal molds with an increase in mold weight due to an increase in wall thickness. Molds in group 3 were all direct-metal molds with the same wall thickness as those in group 2, while group 4 contains molds made from cupola metal and with a weight and wall thickness similar to those in group 2.

Comparing group 1 with group 2 shows a decided decrease in mold life, in spite of an increase in weight. Average manganese content shows a considerable drop, which apparently explains the decrease in mold life, although usually cupola-metal molds (of which group 2 is composed) of analyses similar to direct metal show a lower average mold life. Comparing group 3 with group 1, shows a decided increase in mold life, due to an increase in mold weight and in spite of a lower manganese content. This is probably due to the increased weight plus the advantage of direct metal. A much more marked increase is shown by comparing group 2 with group 3. The metal analyses of these two groups is similar but the molds in group 3 were cast from direct metal while those in group 2 were

made from cupola metal. Group 4, as compared with group 3, gives a good idea of the value of direct metal. The metal analyses in these two groups is similar but group 4 (cupola metal) shows a decrease in average mold life..

Fig. 10 pictures the mold life of two large groups of molds, one group containing 24 and the other 25 molds. It pictures strikingly the difference between direct-metal molds and cupola-metal molds, and also the difference between high and low manganese. The direct-metal group

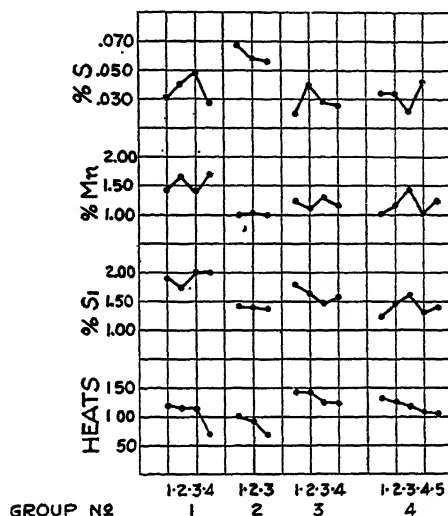


FIG. 9.—LIFE OF DIRECT-METAL AND CUPOLA-METAL 24-INCH FLUTED INGOT MOLD.  
*Mold Life and Analysis*

Group No.	Type of Metal	Mold Weight, Lb.	Number of Heats	Average Metal Analyses, Per Cent		
				Mn	Si	S
1	direct	16,300	106	1.51	1.92	0.037
2	cupola	17,800	87	1.00	1.38	0.060
3	direct	17,800	135	1.19	1.60	0.028
4	cupola	17,800	119	1.17	1.38	0.033

with a much higher manganese content shows an increase in mold life over the cupola-metal group (No. 5) of about 26 per cent. It is interesting to note that the much higher silicon on the right-hand end of the graph for group 3 would indicate that when the silicon content is 1.60 per cent or higher, it apparently has an appreciable effect in reducing mold life.

The reason for using such a large percentage of cupola-metal molds in this type of practice is the ability to cast the cupola metal to a much closer tolerance than the direct metal, and for this type of work accurate ingot size is a very important factor. The two groups of molds shown on Fig. 11 show generally what can be expected from groups of molds

made from direct metal, as compared with similar molds made from cupola metal. In this case the manganese content of the cupola-metal molds is much lower, 0.95 per cent as compared to 1.55 per cent for the direct-metal molds.

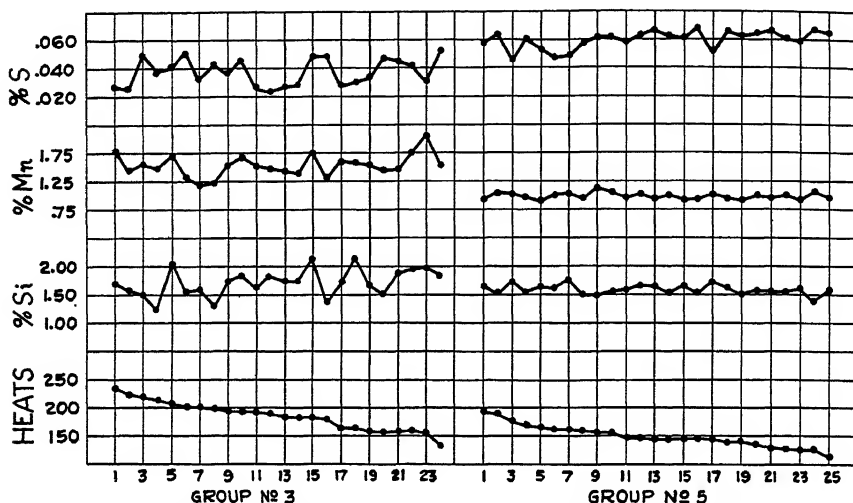


FIG. 10.—DIFFERENCE BETWEEN DIRECT-METAL AND CUPOLA-METAL MOLDS; ALSO DIFFERENCE BETWEEN HIGH AND LOW MANGANESE.  
*Mold Life and Analysis*

Group No.	Type of Metal	Mold Weight, Lb.	Average No. of Heats	Average Metal Analyses, Per Cent		
				Mn	Si	S
3	direct	15,580	190	1.55	1.72	0.038
5	cupola	15,300	150	0.95	1.59	0.060

### VARIOUS FACTORS

Undoubtedly, factors other than chemical analyses and wall thickness have considerable influence upon mold life. In a great many of the groups presented, casting temperatures were similar, or at least an attempt was made to maintain casting temperatures at a given figure. Brearley<sup>1</sup> says that "hot casting in the aggregate is the chief variable in the life of cast-iron molds." Other factors seem to be of greater importance, especially when casting temperatures are held to a figure that is accepted as good practice.

Owing to the similarity of all the various sizes of molds presented in this study, it is felt that mold design may be eliminated as one of the variables in this study. Mold design, however, is often reflected in wall

<sup>1</sup> A. W. and H. Brearley: *Ingot and Ingot Moulds*, 92. London, New York, 1918. Longmans, Green & Co.]

thickness. Nelson<sup>2</sup> says: "the effect of heaviness of mold wall on cooling strains is a much more important factor in choosing the proper mold than the effect of mold wall on the rate of solidification." In reducing wall thickness to a minimum to reduce the effect of cooling strains, ingot-mold life is also reduced. Just where the happy medium is that gives minimum effects from cooling strains and maximum mold life can only be determined by constant attention to mold design correlated with rolling and forging practice.

Another factor that perhaps has considerable effect upon mold life is carbon, particularly combined carbon. The percentage error in the chemical analyses for combined carbon is considerable. The difficulty in sampling a mold for combined carbon, the variation due to segregation, etc., adds to this percentage of error. While some figures are available showing the effect of carbon upon mold life, nothing definite has been obtained. Some are of the opinion that the combined carbon should be reduced to a very low figure to give maximum mold life. This idea does not seem to check with some work done by our English friends. They have developed a heat-resisting iron, low in total carbon, high in silicon, and of almost negligible combined carbon content. It is known as "Silal" iron, but it is specifically stated that this material is not recommended for ingot molds<sup>3</sup>.

It would be interesting to compare in detail mold structures from material made from direct metal with similar structures cast from cupola metal, to determine if possible why direct-metal molds with similar metal analyses have so much better mold life. Perhaps the "condition in which the carbon, particularly the graphite, exists in pig iron<sup>4</sup>," is the cause of the variation. Apparently Mr. Clair was able to get away from his difficulties by his method of controlled cooling of the pig metal. Some work has been done on the structure of mold iron. Of particular interest is the work of the Iron and Steel Institute in the study of the heterogeneity of steel ingots<sup>5</sup>, but that work does not indicate anything of value in correlating mold structures with mold life, although the statement is made that it is virtually impossible to correlate mold life with chemical composition. The mold analysis shown in this British report is interesting because it differs widely from the analysis found in mold materials in this country (Table 2). Samples 3A and 3B were from a mold after it had been in service and had failed. Little mention is made

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<sup>2</sup> Nelson: Solidification of Steel in Ingot Molds. *Trans. Amer. Soc. for Metals* (1934) **22**, 211.

<sup>3</sup> Ingot Mould Material. 4th Report on Heterogeneity of Steel Ingots, Iron and Steel Inst., sec. 6, pt. 1, 131.

<sup>4</sup> E. L. Clair: Discussion on Qualities of Pig Iron. *Trans. A.I.M.E.* (1936) **120**, 159 et seq.

<sup>5</sup> Reference of footnote 3, 129-161.

of mold life but from the meager figures given it would indicate (as compared with practice in the United States) that very low mold life is obtained. Perhaps the very low mold life is due to the very low manga-

TABLE 2.—*Typical Analysis of English Ingot Molds*

Mold No.	Total Carbon	Combined Carbon	Graphitic Carbon	Silicon	Manganese	Sulfur	Phosphorus
1	3.77	0.82	2.95	1.81	0.43	0.096	0.037
2	3.48	0.74	2.74	2.08	0.74	0.039	0.042
3A	3.43	0.83	2.60	2.46	0.78	0.083	0.029
3B	3.57	0.77	2.80	2.20	0.74	0.032	0.039

nese content and to the very high silicon content. The figures in Table 2 for mold analyses seem to be similar to those quoted in Brearley's work on ingot molds<sup>6</sup>.

### SUMMARY

Based upon the data presented, an attempt has been made to determine the chemical analysis that gives maximum mold life. Mold-life

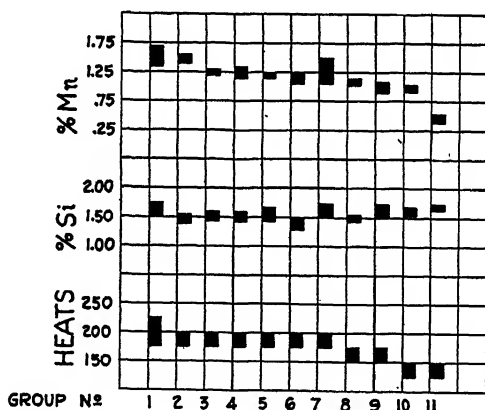


FIG. 11.—CHEMICAL ANALYSIS THAT GIVES MAXIMUM MOLD LIFE.

figures, together with chemical analyses, etc., have been tabulated in Table 3. To obtain these figures, the molds on the ends of the various graphs giving maximum mold life have been selected, together with their corresponding approximate analyses. These figures have been plotted in Fig. 11, in which it can be seen that as manganese content decreases mold life also decreases, and also as silicon increases above a certain figure, mold life also decreases. The one group of molds with the best life of any of the groups presented is the group of molds numbered from 1 to 10, shown in group 3 in Fig. 10. The approximate analyses of these

<sup>6</sup> Reference of footnote 1.

molds shows them to contain from 1.35 to 1.65 per cent manganese and from 1.50 to 1.75 per cent silicon. The average life of this group of molds is about 210 heats. It should also be noted (Table 1) that the ratio of ingot weight to mold weight is somewhat higher for this particular size of mold (1.96) than for some of the other sizes discussed, which would indicate that a combination of proper ratio of ingot weight to mold weight plus the proper chemical analyses is the correct combination for maximum mold life. Apparently the higher manganese contents are conducive to long ingot-mold life.

TABLE 3.—*Summary of Data*

Group No.	Fig. No.	Group No.	Size, In.	Best Life, Heats	Best Silicon Content, Per Cent	Best Manganese Content, Per Cent	Weight, Lb.
1	10	3	21	175-225	1.50-1.75	1.35-1.70	15,580
2	7	4	20	175-200	1.40-1.55	1.40-1.55	13,000
3	5	3	18	175-200	1.45-1.60	1.20-1.30	11,100
4	6	1	17	175-200	1.45-1.60	1.15-1.35	10,400
5	6	2	17	175-200	1.45-1.70	1.15-1.25	10,400
6	8	8	21	175-200	1.30-1.50	1.05-1.25	15,300
7	7	5	20	175-200	1.50-1.75	1.05-1.50	13,000
8	5	2	18	150-175	1.45-1.55	1.00-1.10	13,300
9	10	5	21	150-175	1.50-1.75	0.90-1.10	15,300
10	5	1	18	125-150	1.55-1.70	0.95-1.05	13,470
11	8	10	21	125-150	1.65-1.75	0.40-0.55	15,300

Assuming that for the type of steel being manufactured the ingot mold is of the proper design, it seems safe to predict that for a given type of mold, with casting conditions relatively consistent, two factors affect ingot-mold life: (1) wall thickness or mold weight, and (2) chemical analysis of the metal, particularly manganese. Manganese of approximately 1.50 per cent with silicon of about 1.60 per cent seems to give maximum mold life. Silicon content of over 1.60 per cent results in a shortening of the life.

## DISCUSSION

(G. D. Tranter presiding)

E. J. KAUFFMAN,\* Hubbard, Ohio (written discussion).—Mr. Reagan begins by saying: "In a study of the life of ingot molds, it is essential to eliminate all of the variables." This is a sound statement that the writer has verified by long experience. Just how sound is well shown by listing the major variables involved.

### I. Factors incident to manufacture of ingot mold

#### A. The Mold Metal

1. Type of iron used; i.e., direct, cupola, open hearth
2. Chemical composition
3. Physical nature

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4. Casting temperatures—ladle to molds, and this latter is a function of the type, chemical composition and physical nature of the metal
- B. Workmanship, that is to say, the experience, skill and integrity of the moldmaker
  1. Type of equipment used
  2. Choice and proper use of suitable sand
  3. Annealing
  4. Finishing and intelligent and rigorous inspection of the product
- C. Design
  1. Design of mold as to producing a good ingot
  2. Design of mold in order to obtain maximum mold life consistent with good ingot practice

(It follows, therefore, that the moldmaker and designer must have had experience not only in the founder's art but also in that of the steelmaker as well.)
- II. Variables or factors incident to use or type of service required of mold in steel plant
  - A. Shape and size of mold
    1. Superslab, slab, near square, square, near round and round in sizes ranging from molds weighing 5 lb. to 50 tons or more
  - B. Kinds of steel to be suitably transformed from liquid steel to solid ingot
    1. Open, semiopen, semikilled, killed, and all of the various and too numerous to mention alloy steels
  - C. Other steel-plant conditions as to mold life
    1. Molds are run too hot or too cold. Too many mold sizes, not enough drags, and so on ad infinitum
    2. Top-poured vs. bottom-poured molds
    3. Last, and not least, pouring a mold, just once, too hot takes more out of that mold than twenty normal pourings

Now, to continue, the ingot-mold practice described by Mr. Reagan does eliminate a considerable number of the above enumerated variables. This is a prime requisite when it comes to arriving at any really worth-while information as to the whys and wherefores of mold life. The writer is familiar with the mold practice outlined in Mr. Reagan's paper and is absolutely in accord with his premises.

In Fig. 3, the paper illustrates the type of failure to which the duodecagonal mold described is subject; i.e. heavy fire-cracking on the flats 3 to 6 in. above the bottom radius of the mold. Mr. Reagan suggests that the immediate cause for this is: "Apparently the greatest amount of heat is concentrated at the point of failure." May I suggest that this is also the point at which there exists a certain tendency for the steel entering the bottom of the mold under pressure to swirl and rotate and thus, to a certain extent, wash the bottom wall section of the molds. This, indeed, will cause local concentration of heat partly due to mechanical reasons. It would appear that a greater thickness of mold wall in the lower part of the mold should help. This is apparently true, as upon referring to Fig. 4 we find that: "The first group of 13-in. molds averaged 6100 lb. each and gave an average life of 194 pours. In group 2 the mold weight was increased to 6900 lb. and the mold life was increased to 254 heats." In other words, an addition of 800 lb., or 13.1 per cent to the weight of the mold, increased the life from 194 to 254 pours, or about 31 per cent, assuming all other factors to have been practically the same.

To briefly check Mr. Reagan's summary of the factors strongly affecting mold life under the service conditions outlined:

"First, wall thickness or mold weight." In the writer's opinion this is strictly true, as is well illustrated by the example cited above.

"Second, chemical analysis of the metal, particularly manganese." The writer's experience most definitely agrees with that part of Mr. Reagan's conclusion applying

to manganese. In fact, the writer has checked molds containing as high as 2.5 per cent Mn that gave excellent service. For molds having wall thicknesses in the range described by Mr. Reagan (3.65 to 6.7 in.), I should say that a silicon content of 1.40 to 1.75 per cent is well suited to yield excellent results.

Mr. Reagan has given thoughtful consideration to his subject, and has collected data in his paper that are highly valuable to the art.

C. R. FONDERSMITH,\* Middletown, Ohio (written discussion).—We have no experience of recent date with either this type of mold or grade of steel. More conclusive evidence, of course, will be obtained by Mr. Reagan as more molds are followed in service. Small groups of molds, it would seem, give questionable results. There is room for much study on this problem, as the present mold seems to be the result of rule of thumb where more metal is continually applied at the point of mold failure. Consequently we have been using heavier and heavier molds, compared with the ingot weight. It would seem that it might be possible by applying definite engineering principles to give the steel mill a lighter mold, which might give not only the same mold life but an improved ingot condition.

Our experience has indicated that direct metal molds give a longer average life with the usual variations due to foundry practice in making and of final pouring practice. We feel that even more important than metal analysis is the temperature at which molds are poured in the mold foundry, and it would be interesting to see a correlation of these data. Table 4 gives a spot check taken on 20 molds this past week.

TABLE 4.—*Spot Check on Twenty Molds*

Direct Metal						Cupola Metal					
Mold No.	Composition, Per Cent				No. Heats	Mold No.	Composition, Per Cent				No. Heats
	Mn	P	S	Si			Mn	P	S	Si	
38	1.39	0.151	0.060	1.65	65	6715	1.13	0.204	0.037	1.35	41
23	1.14	0.142	0.049	1.66	90	6626	1.31	0.187	0.049	1.32	64
31			0.058	1.82	93	6567	1.27	0.176	0.034	1.47	70
24	1.26	0.147	0.042	1.72	96	6637	1.27	0.187	0.042	1.49	71
45	0.90	0.155	0.070	1.63	113	6573	1.32	0.174	0.042	1.62	93
43	1.26	0.137	0.050	1.53	119	6439	1.02		0.066	1.43	101
41	1.20	0.140	0.060	1.54	122	6440	1.09	0.198	0.052	1.45	115
37			0.050	1.45	134	6393	1.27	0.145	0.042	1.42	106
11	1.05	0.136	0.042	1.62	134	6422	1.12	0.207	0.034	1.60	116
						5704	1.22	0.203	0.036	1.37	126
						4749	1.30	0.177	0.098	1.24	117
Ingot weight, lb.....12,000						11,000					
Mold weight, lb.....17,400						16,000					

Assuming that with slab molds and top pouring 90 per cent live steel of under 0.10 carbon analysis, there is a possibility of the same conclusion applying; namely, as manganese content decreases, mold life decreases. Best analysis is 1.50 Mn, 1.60 Si—range Mn 135/165, Si 150/175. Silicon over 1.60 shortens life.

\* Superintendent, Open Hearth Department, American Rolling Mill Co.



The variation due to ratio of weight has been eliminated but analysis of these data reveals that for this group of molds on this grade steel the above conclusions do not seem to apply. This has been the history on all our correlations of mold analysis with mold life and further confirm our opinions that within general wide analysis limits the controlling factor is temperature of foundry casting and variation in use.

G. PUTNAM,\* Youngstown, Ohio.—I am not an expert on molds. I think Mr. Reagan's paper is a comprehensive document on the subject of mold life, but it may not cover the situation for all open-hearth men here. I understand that at Edgewater they pour practically all high carbon and bottom-pour, and many open-hearth men attempting to correlate their practice with a practice of that sort are not able to do it. The reason they are not able to do it, of course, is because different classes of steels are made.

One of the most important items that I have been able to find from the standpoint of mold life is the type of service and design that you get from the mold manufacturer. Certainly the mold manufacturers are able to produce a better mold in most cases than the homemade molds. There are a good many plants in the country that do produce their own molds and their mold practice runs upwards to around 50 lb. of mold per ton. There are a number of plants in the country in which various grades of steel are poured, including all the low carbons and some high carbons, some bottom-pour but most of them top-pour, where they run under 25 lb. per ton of steel, which should be regarded as pretty good practice.

The items that I have jotted down here that are most effective on mold life are to some extent a repetition of those mentioned by Mr. Reagan, Mr. Kauffman and Mr. FonDersmith.

I have made no study of mold life with reference to the amount of carbon, graphitic or combined, but I think in the future there will be things discovered with reference to mold life along that line. A sulphur content around 30 to 35 seems to be fairly good. Probably one of the reasons for this is that the metal is fluid at that percentage of analysis and gives a very good casting. A silicon content of about 1.65 seems to be the better. A range of 1.30 to 2 per cent is given. Manganese at around 1.25 is good. Manganese 0.50 to 1 per cent seems to be not so good. Manganese, however, below 0.50 in many cases has worked out satisfactorily. Phosphorus at about 0.100 to 0.135 seems to be the best.

There is one reason why most of the molds made in home foundries are not as good as those made by mold manufacturers. The metal used is metal that is used also in the open hearths and consequently the analysis is not suited to mold manufacture. The mold manufacturer, of course, specifies a certain analysis of metal for molds.

Probably casting temperatures of around 2300° are right.

There is much controversy between direct metal and cupola metal. I have seen high mold life from each but I have never run any averages on the two to see which was the better.

One of the most important considerations, of course, in mold life is the design. Wall thickness and contour, and height with reference to contour, I think, are important. For instance, it is often possible to vary the height of the mold with the same contour and increase the mold life. Taper is an important item but not of such great importance as other things. Mr. FonDersmith touched on one of the most important things; that is, the item of the application of mold-wall thickness at the right point. It is not sufficient simply to increase the weight of the mold at the point where the greatest strain comes. That has been well exemplified in the steel business, by some

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\* Republic Steel Corporation.

of the designs we have improved by increasing mold-wall thickness at the proper point on the wall.

Mold preparation is important. It has been our practice to tar molds. We have tried various methods of preparation, among them graphite, various lacquers, salt dip and water dip. I believe water dip actually increases the life of the mold. I believe salt dip decreases the life of the mold. I cannot see that tar changes the mold life to any degree.

The type of steel being poured has an effect, of course, on the mold life. The fact that some people are running with a smaller number of drags of molds than they should have, and are pouring their molds hot, is very destructive to mold life.

However, the two factors that are most important are the design of the molds and the service obtainable from mold manufacturers in the design of the molds and the application of the knowledge that they build up to the conditions that exist in each plant.

W. J. MERTEN,\* Pittsburgh, Pa.—Is there not a very much more fundamental reason for the results that Mr. Reagan has obtained with these higher manganese ingot-mold castings? The expansion characteristics are improved, of course, by an increase in manganese. Has not the physical condition or density of structure of the mold metal itself a great deal to do with it? Since everybody else finds that manganese is a help, favorable expansion characteristics of the mold material logically attributed to higher manganese and very much higher percentages than Reagan has used should be conducive to better life of molds.

E. J. KAUFFMAN.—I want to make this comment knowing that Mr. Reagan has put a lot of time and work on his paper. I did not want to let one point escape the attention of this meeting. I think the thing that Mr. Reagan has particularly tried to bring out, and which I recognize as being valuable, is that under the conditions of the practice outlined a great many of the factors that ordinarily complicate the evaluation of mold life and the variables affecting it are eliminated. Therefore, the conclusions drawn by Mr. Reagan I believe to be in the main correct.

We have evaluated some thousands of molds but almost always have run against the stone wall, so to speak, of lack of accurate knowledge of service conditions. Molds of a certain analysis may yield splendid results. At a later time period, molds of like analysis used in the same plant did not give anywhere near as good life. We felt that this was caused to a certain extent, at least, by variation in operating conditions, thus making it difficult to arrive at optimum analysis for the best possible mold life.

I do think that the makers of ingot molds of this country, from the contacts I have had with them, are anxious to produce molds that will help the steelmakers, but are often handicapped by difficulties that prevent arriving at just what should be known. Under the mold practice outlined in Mr. Reagan's paper, many of the ordinary service variables are eliminated.

MEMBER.—Has Brinell hardness been taken of mold metal? Is there any relation between original Brinell hardness of the mold and mold life?

E. J. KAUFFMAN.—Yes, we have done work on Brinell hardness. There is a Brinell machine at our place that we would sell. Brinell hardness, of course, does tell one something about the relative hardness or softness of the metal. About 8 or 10 years ago, for a period of two years or more, we cast test bars from each cast of metal. The bars were fractured and Brinelled and attempts made to correlate the results with a great many factors, including mold life. Briefly, the Brinell did not appear to be well adapted as a practical method of control for molds.

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\* Pittsburgh Rolls Corporation.

W. J. MERTEN.—On the question of the carbon content of the mold metal, assuming silicon and phosphorus and the other elements to be the same, which would tend to make the better mold metal, a carbon content of 3.80 per cent—that is, 3.80 total carbon—or a total carbon content of 3.1 per cent?

E. J. KAUFFMAN.—I dislike taking too much time, nor do I wish to go into a long dissertation on the subject of carbon, although as moldmakers we are naturally interested. I do want to say that about two years ago someone at one of these meetings cited two molds; one had a combined carbon content of about 65 or 70 points and the other about 25 or 30 points. The mold with the higher combined carbon was reported as giving a considerably longer life than the mold with less combined carbon, and from this certain deductions were drawn indicating that the higher combined carbon was the reason. Such deductions are not scientific. They are very dangerous for the simple reason that two molds are insufficient, in view of existing variables, to safely permit any definite conclusion. It is difficult to know how much combined carbon is in any given mold because of extreme difficulties as to sampling the mold itself, and assuming that there is an accurate sample, the determination of combined carbon is not easy and is subject to serious errors. What with the difficulties inherent in both sampling and combined carbon determination, the results are not ordinarily accurate within about 10 points either way, and we have plenty of evidence to that effect. I do not mean to say that the combined carbon of ingot molds is not important, but I do mean to say that using only two molds as a basis for a highly important conclusion is nonscientific and, therefore, might lead to incorrect conclusions.

R. C. GOOD,\* Pittsburgh, Pa.—We should bear in mind that the moldmaker is confronted with the use of his product in all kinds of service, particularly with respect to alternate heating cycles. If the molds were subjected to a more regular life the maker could increase the manganese, and in some cases take advantage of the beneficial effects of chrome additions as well.

MEMBER.—Has anyone made tests along that line?

E. J. KAUFFMAN.—Yes, we have made many photomicrographs before the molds were used and after use, and you can find about anything you want, depending upon where you look.

J. W. KINNEAR, JR.,† Munhall, Pa.—Has anyone had any experience in welding defects in ingot molds?

G. D. TRANTER,‡ Middletown, Ohio.—That might offer a possibility if there was a crack in a mold and the surface otherwise was good. The life of a mold might be prolonged by that practice. Do you use just a regular cast-iron welding type?

J. W. KINNEAR, JR.—Mr. Kauffman can explain it better than I can. We had some very large forging ingot molds that were cut by the pouring stream. Mr. Kauffman suggested that we chip the spots out and weld them up. We saved the cost of welding about four times in increased life of the molds.

E. J. KAUFFMAN.—That simply was a case of a large forging mold that unfortunately had been touched up a bit. It was a shame to scrap the mold and I knew that if it were repaired, as customarily is done in plants specializing in the production of forging ingots, a considerable number of pours could be obtained from it.

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† Assistant General Superintendent, Carnegie-Illinois Steel Corporation.

‡ General Superintendent, Middletown Division, American Rolling Mill Co.

G. D. TRANTER.—Was it a surface repair or crack?

E. J. KAUFFMAN.—No, it was not cracked; it was a surface repair.

A. H. SOMMER,\* Peoria, Ill.—To bear out what some of the operating men have said, that they felt that the usage and the treatment of the mold was really more important than the analysis, I can volunteer this information. We increased the size of our furnaces to the extent that we were about one string of molds short of having enough to keep the molds at about the temperature we thought they ought to be. By adding another string we decreased our pounds of molds and stools used per ton of ingots cast from 34 to 27 lb., or a decrease of about 20 per cent with no other change at all. I am inclined to feel that the treatment the molds get has far more to do with their life than the analysis. I do not mean to say that the work that has been done by Mr. Reagan is not beneficial, but after all there are very few plants that operate under similar conditions to those upon which Mr. Reagan's paper was based.

W. J. REAGAN (written discussion).—As has been noted in the paper, we have attempted to eliminate all possible variables in this study of ingot-mold life. There is no question that the treatment ingot molds receive in plant practice (abusive treatment, in many plants) is not conducive to long ingot-mold life. Long mold life means lower mold cost and any factors that will reduce this cost, within practical limits of course, should certainly be employed.

Much is yet to be learned about ingot-mold design and its effect upon the life of molds and ingot structure, and it is hoped that this paper will serve as a stimulus for further study along this line.

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\* Keystone Steel and Wire Co.

## Rate of Solidification of Rimming Ingots

BY JOHN CHIPMAN\* AND C. R. FONDERSMITH,† MEMBERS A.I.M.E.

(New York Meeting, February, 1937)

IN the manufacture of rimming steel—which constitutes the bulk of the world's production of mild steel—the factors that determine the quality of the product are very closely associated with the pouring and solidification of the steel in the ingot mold. The behavior of the metal in the mold is, on the one hand, the resultant of the complex processes through which the liquid metal has passed, and, on the other, it is an indication of the probable behavior of the ingot during subsequent rolling and finishing operations. A detailed study of the mechanism of solidification of rimming ingots ought to yield information that will be useful in controlling the structure of the ingot and the quality of the ultimate product. The first step in such a study is to determine the rate at which the solid shell of the ingot forms from the liquid metal in the mold. A knowledge of the rate of solidification will make it possible to correlate observations of rimming action and gas evolution with studies of the structure, porosity, and segregation within the ingot.

Thus, if the metal in the mold is observed to fall, let us say one minute after pouring, the portion of the structure associated with this fall will be located in the part of the ingot that is solidifying at that particular moment. The knowledge that the ingot solidifies to a depth of  $\frac{3}{4}$  in. in the first minute enables us to locate in the ingot the structural features corresponding to the observed fall. Conversely, the blowhole condition associated with a rising or growing ingot will be found in the part of the ingot that is solidifying at the time the phenomenon occurs.

The time required for the complete solidification of an ingot has long been a matter of speculation. It is of considerable practical importance in connection with charging and heating in the soaking pits. Too rapid handling of the ingot through heating and rolling processes has been thought to be associated with excessive pipe and other internal defects, so that a further object of this investigation was to attempt to estimate the time required for complete solidification, or the minimum practical time within which the subsequent operations can be performed with the minimum hazard.

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† Superintendent, Open Hearth Department, The American Rolling Mill Co.

A number of investigations, both experimental and mathematical, have contributed to our knowledge of the varied phenomena attending the solidification of steel ingots. The first theoretical treatment of the rate of solidification was published by A. L. Feild<sup>1</sup>, who showed that when liquid metal at its solidification temperature is brought into contact with the mold the thickness  $D$  of the solidified layer at any time  $t$  measured from the instant of contact is given by the formula

$$D = k\sqrt{t} \quad [1]$$

when  $k$  is a constant determined by the physical and thermal properties of the liquid metal and the mold. In a recent exhaustive mathematical treatise on the subject, Schwarz<sup>2</sup> has obtained an apparently reliable estimate of the effects of such variables as metal temperature and the temperature, thickness and thermal conductivity of the mold upon solidification rates. Experimental studies have been reported by Leitner<sup>3</sup>, Lightfoot<sup>4</sup>, and Nelson<sup>5</sup>, in each of which the emphasis was placed upon the solidification of killed steel.

#### METHOD

The simplest and most direct approach to the problem is obtained

by spilling the liquid contents of the ingot at a definite time after pouring, and measuring the thickness of the solidified shell. This is the method employed by Nelson in his study of the rate of solidification of killed ingots. In order to keep down the cost of the investigation, it was decided to employ ingot butts for the preliminary measurements, and later to check these results by spilling a limited number of full ingots. The mold size selected for the experiment was an 18 by 39-in. straight-side mold, having a thickness of 8 in. at the bottom, and normally poured to a

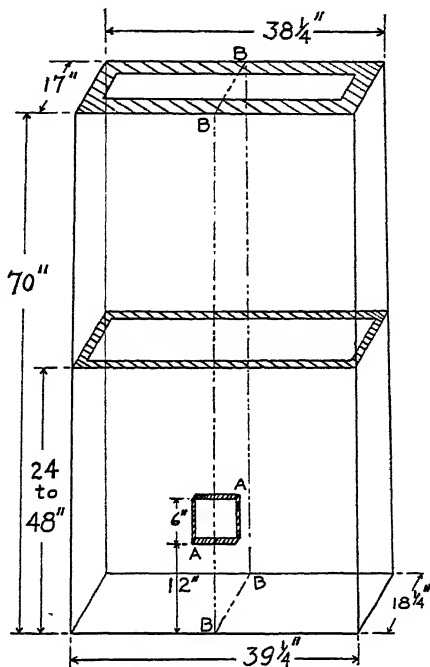


FIG. 1.—METHOD OF SAMPLING INGOT SHELLS.

AA, sample cut from ingot butt; BBBB, line along which ingot shells were split.

<sup>1</sup> A. L. Feild: *Trans. Amer. Soc. Steel Treat.* (1926).

<sup>2</sup> C. Schwarz: *Archiv Eisenhüttenwesen* (1931) **5**, 139-148 and 177-191.

<sup>3</sup> F. Leitner: *Stahl und Eisen* (1926) **46**, 526; (1930) **50**, 1082.

<sup>4</sup> N. M. H. Lightfoot: *Jnl. Iron and Steel Inst.* (1929) **119**, 364.

<sup>5</sup> L. H. Nelson: *Trans. Amer. Soc. Steel Treat.* (1934) **22**, 193.

height of 70 in. The ingot butts used in this study were from 24 to 48 in. high. The time from beginning to pour the butt until the stream was shut off, and the time when the butt was spilled, were all recorded on the stop watch. After the shell had cooled, a piece 6 in. square was cut out with the torch at a height of 12 to 18 in. from the bottom. The position of this piece in the ingot is shown more clearly in Fig. 1. The maximum thickness of this piece was recorded, while the time corresponding was the

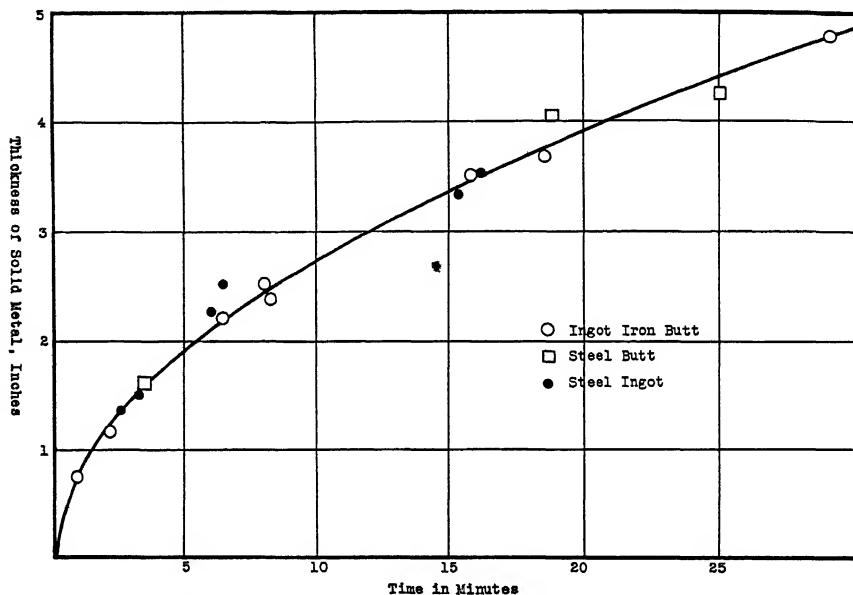


FIG. 2.—RATE OF SOLIDIFICATION OF 18 BY 39-IN. RIMMING INGOTS. Open circles indicate ingot-iron butts; squares, steel butts; solid circles, steel ingots.

time that the metal had been in actual contact with the mold at the height under observation.

The shells of three full ingots that were studied were split longitudinally and the thickness was measured 18 in. from the bottom and the same distance down from the top. On account of the time required to fill the mold and to spill its liquid contents, the times of contact at these two heights differ by about one-half minute. The observed thicknesses also differed slightly; therefore each full ingot studied is represented on the curves by two points.

## RESULTS

The original record of individual experiments containing mold temperatures and other pertinent data was lost in an explosion, which destroyed some of the files of the Research Laboratories. However, a large-scale plot of the data was recovered, and the points shown in Fig. 2 are reproduced from this plot. In general, mold temperatures were

between 150° and 200° F., and the metal temperature was from 70° to 120° F. above the solidification temperature.

According to equation 1, the rate of solidification is proportional to the square root of the time, and the curve of Fig. 2 is drawn in accordance with this simple theory. The relationship is more clearly evident in Fig. 3, in which the thickness of the shell is plotted against the square root of the time of contact. The straight line shows that Feild's<sup>6</sup> equation is valid up to 30 min. The data are adequately represented by the

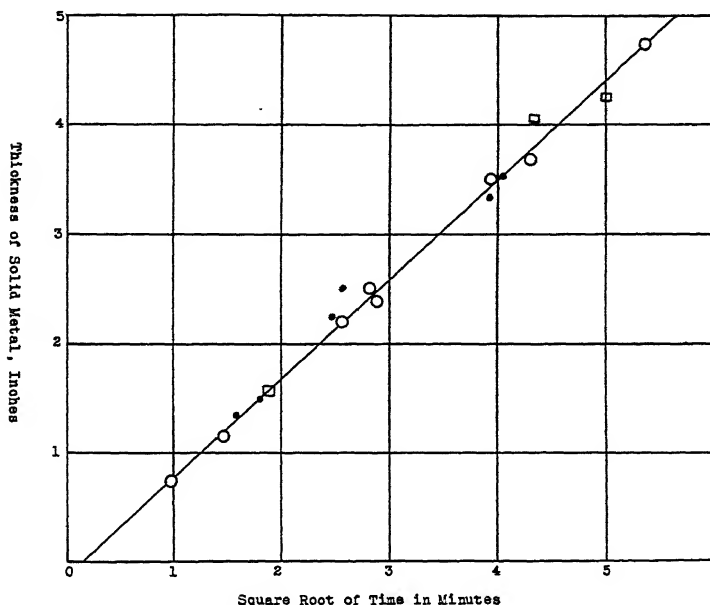


FIG. 3.—THICKNESS OF SKIN PLOTTED AGAINST SQUARE ROOT OF TIME.

equation  $D = -0.12 + 0.9 \times \sqrt{t}$  where  $D$  is the thickness in inches and  $t$  is the time in minutes. The negative first term of the equation implies that there is a lapse of time of about two seconds between the moment of contact and the beginning of solidification. It is doubtful whether our observations are sufficiently accurate to warrant the acceptance of this as a quantitative conclusion.

Several grades of steel were used in this investigation, including plain carbon grades, copper-bearing steel, deep-drawing grades, and ingot iron. All of these are below 0.10 per cent carbon. The ingot iron and steel grades are distinguished by different symbols in Figs. 2 and 3, and it is evident that there is no consistent difference between the solidification rate of steel and that of ingot iron. Nor does the rate for a full ingot poured near the first of the heat differ from that of a last-poured butt. The minor variations from the average curve are probably associated with

<sup>6</sup> See footnote 1.



differences in mold and metal temperatures. Only one ingot of a size different from that mentioned above was used, and this was a 20 by 22-in. ingot of slightly thinner mold-wall section. This was the first experiment of the investigation, and the timing was probably less accurate than in later tests. The results are very slightly above the average curve, as shown by the two points at 6 and 6.4 minutes.

Two full ingots of steel were spilled at 3 and 16 minutes, respectively. Sections were cut from the shells and preserved for further study. Photographs of these sections are shown in Figs. 4 and 5. The irregularity at the left of Fig. 5 is simply a small amount of metal that failed to pour out when the mold was upset. Some observations regarding these shells are worthy of especial mention. The thickness of the shell is approximately the same at the top as at the bottom, the slight difference being fully accounted for by the difference in time of contact of metal and mold. The top of the ingot is free from blowholes, while the bottom contains the characteristic honeycomb structure always found in rimming-steel ingots. The blowholes have evidently had no influence whatever upon the rate of solidification.

Minor irregularities in thickness are especially noticeable in the thinner shell of Fig. 4. Examination of the ingot skin reveals the fact that the thinner portions of the shell occur at points where the metal-to-mold contact was poorer than the average, owing to irregularities in ingot skin or mold surface. These irregularities tend to smooth out as the shell becomes thicker, indicating that after the formation of the air gap between ingot and mold the transfer of heat becomes independent of irregularities of surface. The shell thicknesses used in plotting Figs. 2 and 3 represent the thicker portions of the shell where there was good initial contact between metal and mold.

Attempts were made to follow the course of solidification beyond 30 min. In order to do this, it was necessary to play a stream of oxygen upon the surface of the ingot so as to keep it open, and this apparently retarded solidification in the upper portion of the ingot. At the same time, however, it appeared that a considerable amount of mushy or semi-solid metal accumulated in the lower part of the ingot, which prevented the outflow of liquid metal when the mold was upset. For this reason no accurate estimate could be made of the relationship between time and thickness of shell beyond the 30-min. period. The best estimate we can obtain of the time required for complete solidification is, therefore, by extrapolation of the data represented in Figs. 2 and 3. The results indicate that for an ingot of rectangular cross section 18 in. thick the time required for complete solidification is approximately 100 min. The effect of stripping before the expiration of this time would be to hasten the solidification, whereas charging into the pits would probably retard it. In handling an ingot before the expiration of the full solidification time,

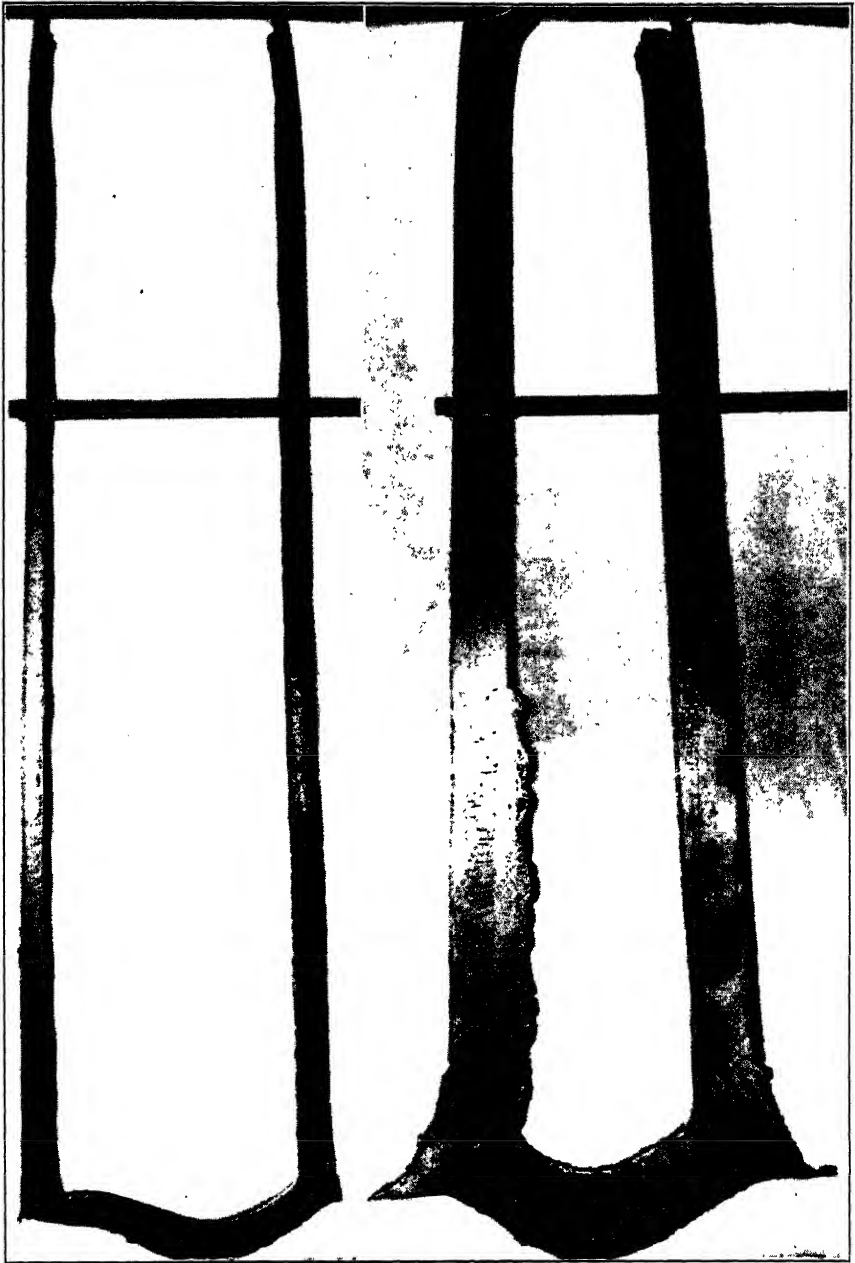


FIG. 4.

FIG. 5.

FIG. 4.—SKIN OF INGOT OF LOW-CARBON STEEL SPILLED THREE MINUTES AFTER STARTING TO POUR.

FIG. 5.—SKIN OF INGOT OF LOW-CARBON STEEL SPILLED SIXTEEN MINUTES AFTER STARTING TO POUR.

the liquid or mushy nature of its center must be borne in mind and precautions taken against damaging its internal structure.

### SUMMARY

The rate of solidification of rimming ingots has been determined by spilling the liquid contents and measuring the thickness of the solidified wall. Within the grades studied, which were all below 0.10 per cent carbon, the rate is the same. The thickness solidified at various times was:

Time, min.....	1	2	3	5	10	15	20	25	30
Thickness, in.....	0.78	1.15	1.44	1.89	2.73	3.36	3.90	4.38	4.81

### ACKNOWLEDGMENTS

The authors express their thanks to Mr. E. D. Buchanan, Mr. J. Spang and Mr. Shadburn Marshall for their cooperation in this study.

### DISCUSSION

[See also page 349]

(*L. F. Reinartz presiding*)

L. F. REINARTZ,\* Middletown, Ohio.—Our British friends theorize a good deal about what is happening on the inside of a rimmed-steel ingot, and they have had the idea that a rimmed-steel ingot solidifies much more rapidly at the bottom than at the top. I think these experiments have clearly demonstrated that the rate of freezing is almost the same at the bottom as at the top.

In England operators discussed the possibility of pouring out the inside of an ingot, making a solid rim that could be used for the manufacture of pipe. They were afraid that the thickness of the wall at the top would differ so much from that at the bottom that it could not be used.

J. CHIPMAN.—In the equation  $D = -0.12 + 0.9 \times \sqrt{t}$  on page 373, we do not know where the 0.12 comes from. It is probable that the measurements are not made with sufficient accuracy to distinguish 0.12 in., but that fitted the curve much better than if the first term had been zero. The thinnest skin we measured was something like  $\frac{3}{4}$  in. thick. It was an ingot spilled 55 sec. after it was poured, and it takes pretty fast going to get the ladle away and get another crane up to spill the ingot 55 sec. after it is poured. The steel referred to here is low-carbon rimming steel below 0.10 carbon, and it was surprising to us that it should fall so close to the line that represents ingot iron.

W. J. REAGAN,† Oakmont, Pa.—May I ask if those data have been accumulated for any other ingot size than the one shown, or any other wall thickness?

C. R. FONDERSMITH.—Except for that one ingot that we took, our first ingot was 20 by 30, and the rest were all 18 by 39.

C. H. HERTY, JR.,‡ Bethlehem, Pa.—Did you get a chance to pour any heats that were exceptionally hot to see what the rate was on the very hot heat? We have made

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\* Works Manager, American Rolling Mill Co.

† Open Hearth Department, Edgewater Steel Co.

‡ Research Engineer, Bethlehem Steel Co.

some calculations on this same subject, and the factor that I got in quite a hot heat was 0.8 times the square root of  $t$ .

J. CHIPMAN.—Your coefficient would vary with the different types of ingot, with the different mold thicknesses, perhaps. We have made no experiment on very hot heats. It happens that the two heats that were represented by full ingots were normal temperature heats, and although some of the heats from which we poured butts were on the hot side, by the time the butt is reached it can no longer be considered a hot heat, even though it started out as one.

J. H. NEAD,\* East Chicago, Ind.—I would like to ask Mr. FonDersmith if that ingot, having been poured 16 min., was ready to be capped? It seemed as though the secondary blowholes were starting, yet those might have been from some of the metal that was still left in there.

C. R. FONDERSMITH.—From the way it looked to me, it was just about the time that we would start to cap it.

MEMBER.—In regard to that formula, if you took  $D$  for a radius, I think that would correspond rather closely with our practice on centrifugal casting. I do not remember the exact figures, but I think that our casting of 10-in. diameter would be in the mold 20 or 25 min. If you take that past 25 min., that formula would give the wall thickness that would be the radius and not the diameter.

J. CHIPMAN.—I think there you are dealing with the solidification of a cylindrical object in which the metal for heat dissipation is progressively larger as the heat goes out, whereas with these ingots we have a long, flat side of the ingot and the rate of solidification is essentially that of a liquid metal in contact with the mold wall at an infinite plane of interface, so that the actual coefficient there carries for a flat wall. For a cylindrical mold it might be quite different; in fact, the results that Nelson published some years ago indicated a different coefficient for different sizes of cylindrical objects. These are plain, flat-sided molds, and the side is so big that the end effect can be neglected. In other words, the radius here is infinite.

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\* Chief Metallurgist, Inland Steel Co.

## Structure of Rimmed-steel Ingots

By T. S. WASHBURN\* AND J. H. NEAD,† MEMBERS A.I.M.E.

(New York Meeting, February, 1937)

THE grades of commercial steel produced in large quantities can be divided into two general types from the standpoint of ingot structure—killed and rimmed. Killed steel covers a wide variety with carbon contents throughout the range of the steel portion of the iron-carbon diagram, and is the kind usually used in the production of alloy steels. Rimmed steel is normally associated with carbon ranges under 0.30 per cent, and is not yet used to a large extent in alloy practice, except for copper-bearing steels.

The fundamental differences in the ingots made from these two types of steel can be seen most easily in Figs. 1 to 7. In the rimmed ingot shown in Figs. 5 to 7 there are two lines of blowholes approximately parallel to the sides and coming together at the top and at the bottom of the ingot. In the killed ingots shown in Figs. 1 to 4 these blowholes are not present. Also, the rimmed ingot has no well defined pipe, as compared to the deep pipe on the killed ingots, and there are numerous primary blowholes in the lower portion of the rimmed ingot perpendicular to the surface and close to it, while on the killed ingot there are no blowholes of this type in the ingot shown in Fig. 1 and very small ones close to the surface in the lower part of the ingot shown in Figs. 2 to 4. With respect to the presence of pipe and the primary blowholes, the structure may vary considerably in both rimmed and killed ingots, therefore these cannot be considered as fundamental structural characteristics differentiating the two types of steel. The primary blowholes in rimmed ingots may be much less pronounced than those in the ingot shown in Figs. 5 to 7—as, for example, in “ingot iron,” which is entirely free from them. An example of a cross section of an ingot-iron ingot is shown on page 16 of “Research and Methods of Analysis of Iron and Steel,” published by the American Rolling Mill Co. (1920). A certain amount of pipe may also occur in rimmed ingots, though it is normally porous and not as well defined or deep as in the killed ingot of Fig. 1. In killed ingots, primary blowholes may occur near the surface, as in Figs. 2 to 4, and

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the size of the pipe may be considerably reduced, particularly in hot-topped steel.

The lines of blowholes parallel to the surfaces, or the secondary blowholes, are a definite characteristic of rimmed ingots and result from the difference in the furnace and pouring practice of this type of steel, as compared to the practice for killed steel. In the processing of killed steel various kinds of deoxidizers are added to the furnace, ladle, or molds, and this deoxidation results in the reduction of most of the iron and manganese oxides with the formation of more stable oxides, which may be partly eliminated from the steel during the processing. The deoxidizing additions also may tend to increase the solubility of the gases in the steel. Consequently, when this type of steel is poured into the molds, very little gas is formed, either from reactions or from gases coming out of solution. The top of the ingot freezes over almost immediately after it is poured, and the ingot solidifies without any reactions that affect the composition of the ingot as a whole. In the processing of rimmed steel, the steel is usually more highly oxidized in the furnace than for the production of killed steel, and only enough deoxidizers are used to maintain the iron and manganese oxide content within certain limits. When this type of steel is poured into the molds a reaction takes place between the carbon and the iron and manganese oxides, with the formation of carbon monoxide gas. The evolution of this gas, together with other gases such as hydrogen and nitrogen, which may come out of solution, results in a "rimming" or boiling action of the steel in the mold during and for an appreciable length of time after pouring the ingot. It is this carbon reaction and the rimming action resulting from the evolution of the gases that cause the distinctive differences in the structure of rimmed and killed ingots.

The solidification of a rimmed ingot can be divided into two periods. During the first period, which lasts from the start of pouring until the cap is placed on the ingot or the top freezes over without artificial cooling, gas is evolved continuously and there is a "rimming" or boiling action in the steel. During this period the portion of the ingot between the surface and the secondary blowhole zone is formed. The second period lasts from the time the top freezes over and the rimming action ceases until the solidification of the ingot is completed. These two periods are associated with certain typical structural characteristics in the ingot, and the nomenclature used in referring to them will be as follows:

**Rim Zone:** the portion of the ingot that solidifies during the first or rimming period.

**Core Zone:** the portion of the ingot that solidifies during the second period, after the ingot is capped.

**Primary Blowholes:** the blowholes in the rim zone, running approximately perpendicular to the surface of the ingot.

Secondary Blowholes: the blowholes between the rim and core zone, which form a line approximately parallel to the surface of the ingot.

Skin: the portion of the rim zone between the surface of the ingot and the point where the primary blowholes begin to form.

The problem of obtaining a satisfactory ingot structure in rimmed steel is an important one, as the various characteristics of the structure are associated closely with the properties of the rolled product. The thickness of the skin and the type of primary blowholes affect the surface of the finished product, and the position and type of the secondary blowholes affect the structure and segregation of the steel, as well as the occurrence of laminations.

### INGOT STRUCTURE

In order to demonstrate the different types of ingot structures, and the effects of some of the variables in the furnace, and pouring practice on these structures, a group of experimental heats has been selected for this study. The first two heats are killed high-carbon steel and semikilled low-carbon steel, which were included for the purpose of comparing the structures of killed and rimmed ingots. The remaining heats are rimmed steel made according to production methods, which show some of the normal variations in ingot structure that are encountered in practice.

The ingot cross sections were all obtained by the dynamite method. In a 24 by 43-in. low-carbon rimmed ingot, a row of holes  $1\frac{3}{8}$  in. in diameter and 6 in. apart was drilled on the center line of the 43-in. side. The depth of the holes was approximately 13 in., or slightly over halfway through the ingot. Each hole was usually charged with  $1\frac{1}{2}$  sticks of 60 per cent gelatin dynamite. The electric detonators were connected in series. After the sticks and caps were in place the holes were tamped with damp clay. Particular care must be taken when blasting, to cover the ingot with a ladle or heavy steel box, to prevent injury from flying fragments.

The FeO shown in the slag analyses is the ferrous oxide content. The analyses for oxides in rimmed ladle or slab specimens were made by Scott's method<sup>1</sup>.

#### *Experiment A. Killed Ingot (High-carbon Steel)*

1. Furnace practice. The bath was deoxidized with 10 per cent ferrosilicon; 80 per cent ferromanganese and 50 per cent ferrosilicon were added to the ladle to meet the specification.

2. Pouring practice. Molds were 27 by 27 in. Not hot-topped. Warm and tar-dipped. Poured 84 in. high. No pyrometer reading. There was a 4000-lb. ladle skull.

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<sup>1</sup> F. W. Scott: Extraction of Slag and Oxide Inclusions in Iron or Steel. *Ind. and Eng. Chem., Anal. Ed.* (Jan. 15, 1932) 4, 121.

3. Ladle analysis: C, 0.95 per cent; Mn, 0.36; P, 0.020; S, 0.026; Si, 0.280.

4. Ingot structure. The ingot was split in half lengthwise. Fig. 1 shows the cross section. There is a well defined pipe and no primary or secondary blowholes.

*Experiment B. Semikilled Ingot (Low-carbon Steel)*

1. Furnace practice. The bath was deoxidized with spiegel 10 min. before tapping. Ferromanganese, ferrotitanium and aluminum were added to the ladle.

2. Pouring practice. Molds were 24 by 43 in. Slightly hot. Tar-dipped. Poured 62 in. high. The deoxidation was completed in the molds with an addition of 5 lb. of aluminum at the top of the ingot. Temperature, 2883° F. Clean ladle.

3. Ladle analysis: C, 0.08 per cent; Mn, 0.46; P, 0.015; S, 0.027.

4. Ingot structure. The ingot was split in half along the 43-in. side. The structure is shown in Figs. 2 to 4. The pipe is 28 in. long and 15 $\frac{3}{4}$  in. wide at the top. There are no secondary blowholes. The primary blowholes are very small and short, and penetrate the surface at scattered points. The primary blowholes disappeared at a distance of 34 in. from the butt.

*Experiment C. Normal Rimmed Ingot*

1. Furnace practice. An addition of spiegel was made to the bath 26 min. before tapping. The bath and slag analyses before the spiegel was added were as follows: C, 0.065 per cent; Mn, 0.12; FeO, 16.2. Ferromanganese and aluminum were added to the ladle.

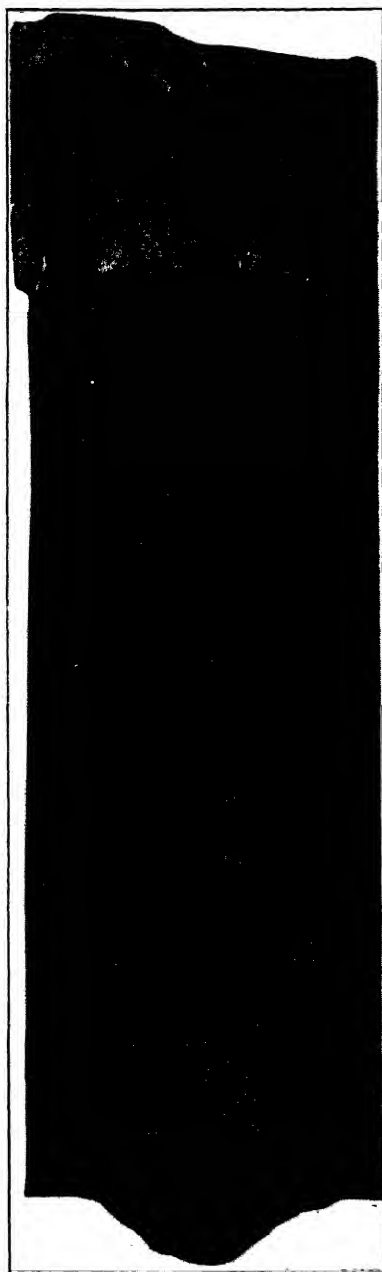
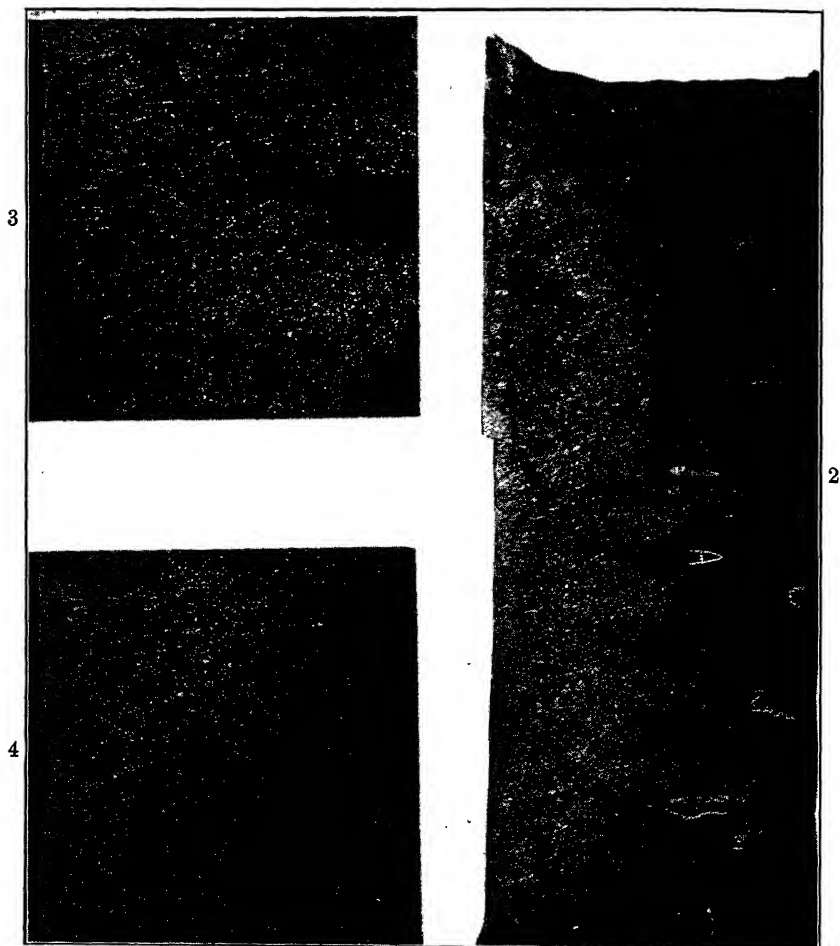


FIG. 1.—CROSS-SECTIONAL STRUCTURE OF KILLED INGOT. ○ EXPERIMENT A. (HIGH-CARBON STEEL.)



2. Pouring practice. Molds were 24 by 43 in. Warm. Tar-dipped. Poured 66 in. high. Eight ounces of aluminum was fed to each ingot during pouring. A good rimming action developed. The metal dropped  $1\frac{1}{2}$  in. before starting to rim, rimmed in  $3\frac{1}{2}$  in. and dropped 2 in., forming a dished top. Temperature, 2894° F.



FIGS. 2-4.—EXPERIMENT B. SEMIKILLED INGOT (LOW-CARBON STEEL).

Fig. 2. Cross-sectional structure of ingot.

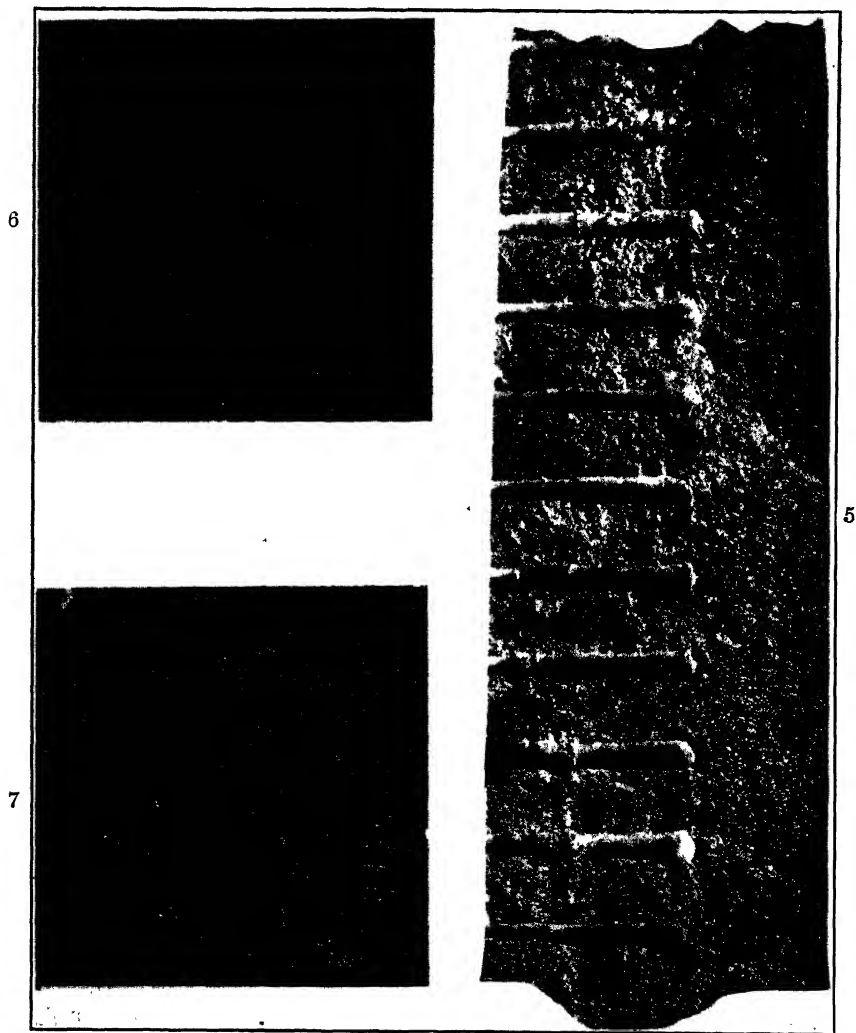
Fig. 3. Enlargement of Fig. 2 showing one side midway between top and bottom.

Fig. 4. Enlargement of Fig. 2 showing bottom corner.

3. Ladle analysis: C, 0.09 per cent; Mn, 0.37; P, 0.009; S, 0.026.

4. Ingot structure. The ingot was split in half along the 43-in. side. The structure is shown in Figs. 5 to 7. The skin is  $\frac{1}{4}$  to  $\frac{1}{2}$  in. thick near the bottom of the ingot. The primary blowholes are of medium size and tend to form a double row in the lower part of the ingot. The row nearest

the surface disappears at a distance of 30 in. from the butt and the inner row disappears at a distance of 40 in. from the butt. The secondary-



FIGS. 5-7.—EXPERIMENT C. NORMAL RIMMED INGOT.

Fig. 5. Cross-sectional structure of ingot.

Fig. 6. Enlargement of Fig. 5 showing one side midway between top and bottom.

Fig. 7. Enlargement of Fig. 5 showing bottom corner.

blowhole zone consists of medium sized blowholes. This zone is approximately 6 in. from the surface.

#### *Experiment D. Thin-skinned Rimmed Ingots*

1. Furnace practice. An addition of spiegel was made to the bath 23 min. before tapping. The bath analysis of a test killed with an excess

of aluminum and the slag analysis before the spiegel was added were as follows: Bath: C, 0.08 per cent; Mn, 0.15; P, 0.011; S, 0.023;  $\text{Al}_2\text{O}_3$ , 0.098. Slag: FeO, 18.1;  $\text{Fe}_2\text{O}_3$ , 8.2. The analyses of similar tests taken 4 min. before the heat was tapped were as follows: Bath: C, 0.09 per cent; Mn, 0.19; P, 0.012; S, 0.020;  $\text{Al}_2\text{O}_3$ , 0.106. Slag: FeO, 18.6;  $\text{Fe}_2\text{O}_3$ , 7.9. Ferromanganese and 42 lb. of aluminum were added to the ladle.

2. Pouring practice. Molds were 24 by 43 in. Warm and tar-dipped. Poured 67 in. high. Three ounces of aluminum was placed on the stool and 5 oz. was added at the top. The metal was slightly wild during the pouring of the upper quarter. There was a 1-in. drop and no growth, with a moderate rimming action, forming a flat top. Temperature, 2916° F. Scrappy ladle.

3. Ladle and slab analyses. Aluminum-killed ladle test: C, 0.09 per cent; Mn, 0.42; P, 0.010; S, 0.020;  $\text{Al}_2\text{O}_3$ , 0.105; Al, 0.572.

Rimmed ladle test:  $\text{SiO}_2$ , 0.0041 per cent;  $\text{Al}_2\text{O}_3$ , 0.0068; MnO, 0.0090; FeO, 0.0317; (FeMn)S plus oxides, 0.107.

Slab tests from middle of ingot:

	$\text{SiO}_2$ , PER CENT	$\text{Al}_2\text{O}_3$ , PER CENT	MnO, PER CENT	FeO, PER CENT	(FeMn)S + OXIDES, PER CENT
Edge.....	0.0005	0.0087	0.0041	0.0213	0.076
Center.....	0.0009	0.0039	0.0025	0.0126	0.098

4. Ingot structure. The ingot was split in half along the 43-in. side. The structure is shown in Figs. 8 to 10. The skin is  $\frac{1}{8}$  to  $\frac{1}{4}$  in. thick near the bottom of the ingot. The primary blowholes are large, particularly those nearest the skin. The primary-blowhole zone disappears about 40 in. from the butt of the ingot, but the blowholes are still fairly large at a distance of 32 in. from the butt. The secondary-blowhole zone consists of medium sized blowholes. This zone is approximately 6 in. from the surface.

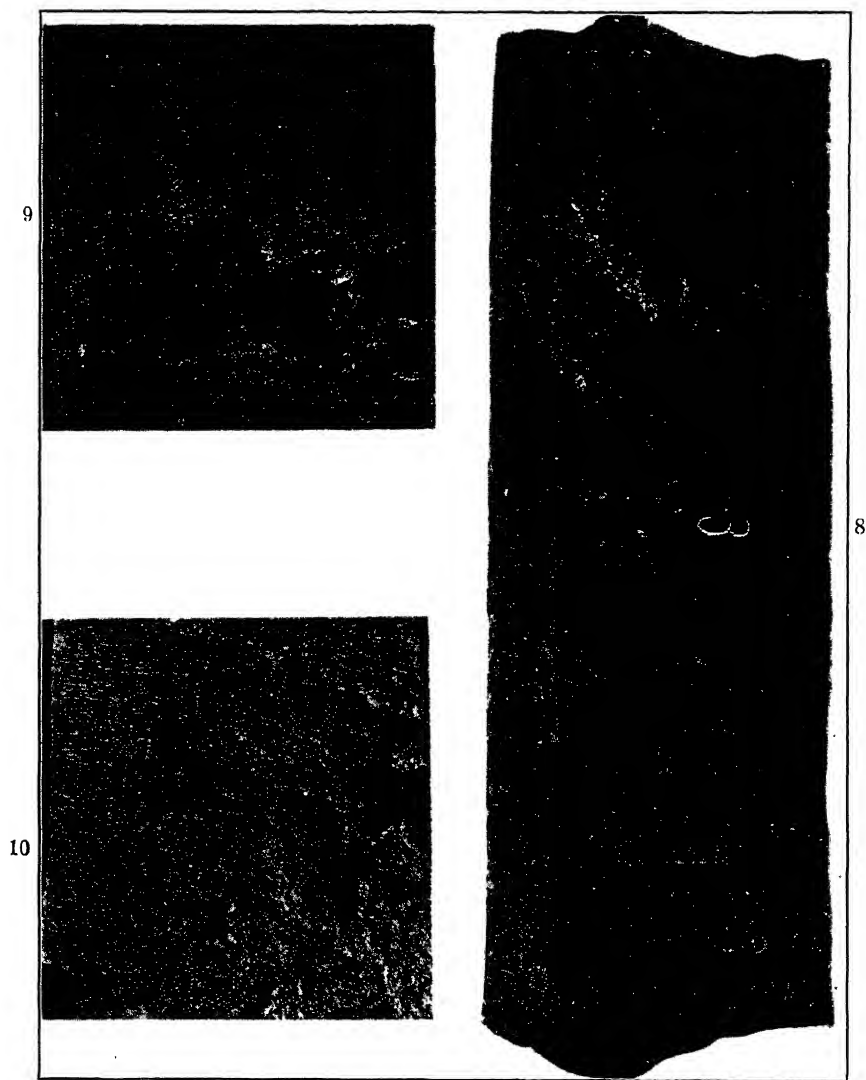
#### *Experiment E. Thick-skinned Rimmed Ingot*

1. Furnace practice. An addition of spiegel was made to the bath 26 min. before tapping. The bath analyses of a test killed with an excess of aluminum and the slag analyses before the spiegel was added were as follows: Bath: C, 0.06 per cent; Mn, 0.14; P, 0.010; S, 0.023;  $\text{Al}_2\text{O}_3$ , 0.122. Slag: FeO, 18.1;  $\text{Fe}_2\text{O}_3$ , 8.6. The analysis of similar tests taken 1 min. before the heat was tapped were as follows: Bath: C, 0.06 per cent; Mn, 0.18; P, 0.009; S, 0.022;  $\text{Al}_2\text{O}_3$ , 0.122. Slag: FeO, 18.8;  $\text{Fe}_2\text{O}_3$ , 8.4.

Ferromanganese and 27 lb. of aluminum were added to the ladle.

2. Pouring practice. Molds were 24 by 43 in. Warm and not tar-dipped. Poured 66 in. high. Three ounces of aluminum was placed on the stool, 2 oz. was added when the mold was one-fourth full, and 3 oz. was added at the top. The metal was wild during topping off. There

was no drop or rise, and a strong rimming action developed, forming a flat top. Temperature, 2899° F. Scrappy ladle.



FIGS. 8-10.—EXPERIMENT D. THIN-SKINNED RIMMED INGOT.

Fig. 8. Cross-sectional structure of ingot.

Fig. 9. Enlargement of Fig. 8 showing one side midway between top and bottom.

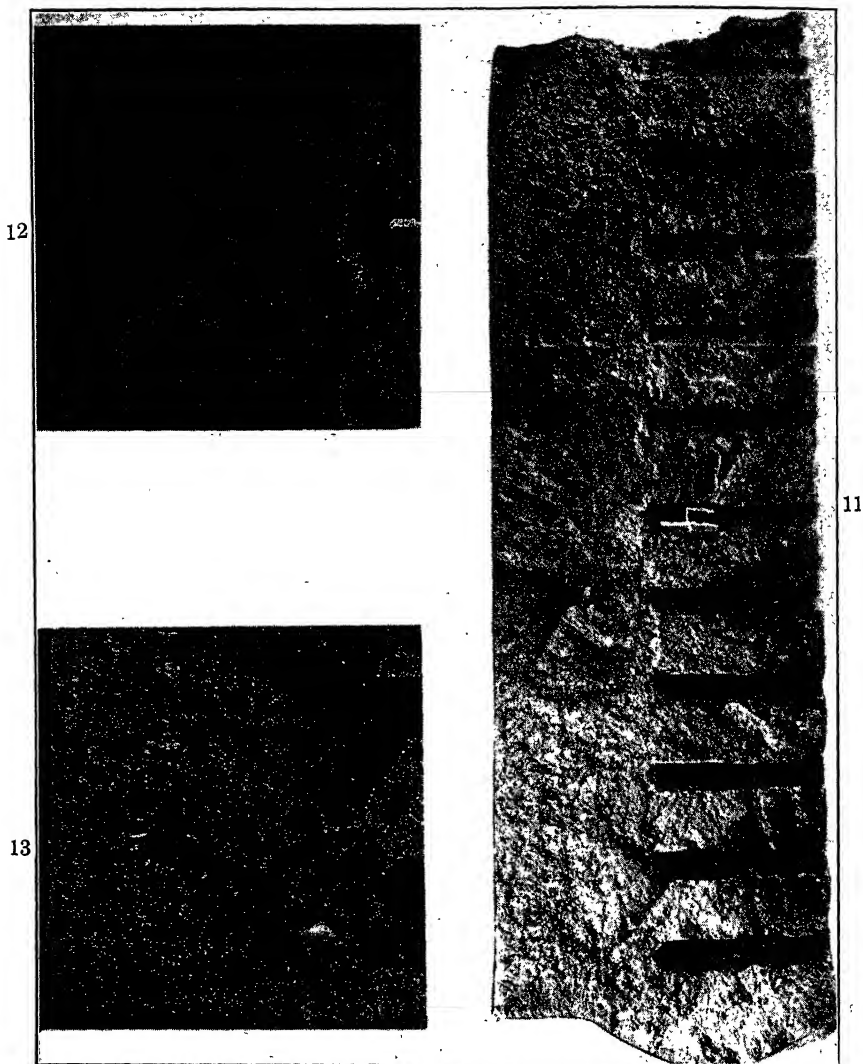
Fig. 10. Enlargement of Fig. 8 showing bottom corner.

3. Ladle and slab analyses. Aluminum-killed ladle test: C, 0.08 per cent; Mn, 0.36; P, 0.013; S, 0.023;  $\text{Al}_2\text{O}_3$ , 0.100; Al, 0.608.

Rimmed ladle test:  $\text{SiO}_2$ , 0.0012 per cent;  $\text{Al}_2\text{O}_3$ , 0.0039; MnO, 0.0061; FeO, 0.0514; (FeMn)S + oxides, 0.125.

Slab tests from middle of ingot:

	SiO <sub>2</sub> , PER CENT	Al <sub>2</sub> O <sub>3</sub> , PER CENT	MnO, PER CENT	FeO, PER CENT	(FeMn)S + OXIDES PER CENT
Edge.....	0.0006	0.0114	0.0060	0.0149	0.074
Center.....	0.0005	0.0033	0.0034	0.0072	0.097



FIGS. 11-13.—EXPERIMENT E. THICK-SKINNED RIMMED INGOT.

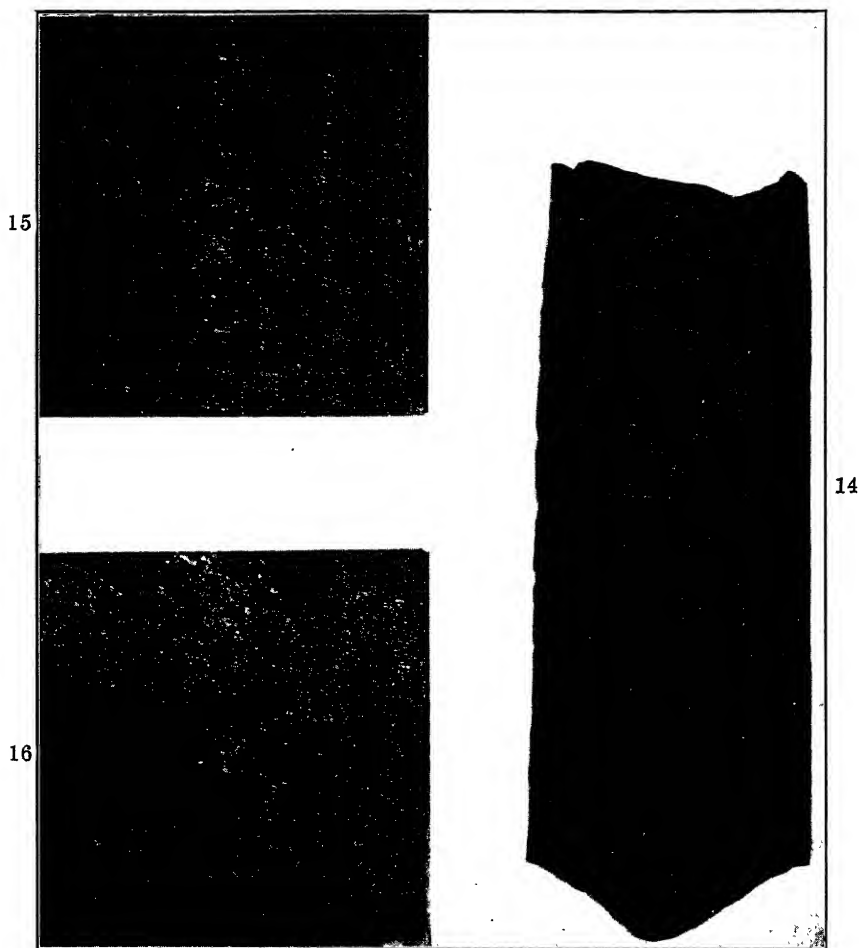
Fig. 11. Cross-sectional structure of ingot.

Fig. 12. Enlargement of Fig. 11 showing one side midway between top and bottom.

Fig. 13. Enlargement of Fig. 11 showing bottom corner.

4. Ingot structure. The ingot was split in half along the 43-in. side. The structure is shown in Figs. 11 to 13. The skin is  $\frac{3}{8}$  to  $\frac{5}{8}$  in. thick

near the bottom of the ingot. The primary blowholes are small. The primary-blowhole zone disappears about 41 in. from the butt. The secondary-blowhole zone consists of medium sized blowholes. This zone is approximately  $4\frac{3}{4}$  in. from the surface.



FIGS. 14-16.—EXPERIMENT F. SHORT RIMMED INGOT.

Fig. 14. Cross-sectional structure of ingot.

Fig. 15. Enlargement of Fig. 14 showing one side midway between top and bottom

Fig. 16. Enlargement of Fig. 14 showing bottom corner.

#### *Experiment F. Long and Short Rimmed Ingots*

1. Furnace practice. An addition of spiegel was made to the bath 32 min. before tapping. The bath and slag analyses before the spiegel was added were as follows: C, 0.06 per cent; Mn, 0.14; FeO, 17.6. Ferro-manganese and 41 lb. of aluminum were added to the ladle.

2. Pouring practice. Molds were 24 by 43 in. Warm and not tar-dipped. Poured 58 and 82 in. high.

For 58-in. ingots, 8 oz. of aluminum was fed during the pour. The metal dropped 2 in. and a strong rimming action developed, forming a slightly dished top.

For 82-in. ingots, 12 oz. of aluminum was fed during the pour. The metal dropped 1 in. and a strong rimming action developed, forming a flat top with a tendency to pyramid a little before capping.

Temperature was 2901° F. There was a 1000-lb. plate in the ladle.

3. Ladle analysis: C, 0.10 per cent; Mn, 0.44; P, 0.008; S, 0.021.

4. Ingot structure. A 58-in. ingot and an 82-in. ingot, which were the eighth and tenth ingots poured, were both split in half along the 43-in. side.

The structure of the 58-in. ingot is shown in Figs. 14 to 16. The skin is  $\frac{1}{4}$  to  $\frac{3}{8}$  in. thick near the bottom of the ingot. The primary blowholes are small and form a double row. The primary-blowhole zone disappears about 34 in. from the butt. The secondary-blowhole zone consists of medium sized blowholes. This zone is approximately  $5\frac{3}{8}$  in. from the surface.

The structure of the 82-in. ingot is shown in Figs. 17 to 19. The skin is  $\frac{1}{4}$  to  $\frac{3}{8}$  in. thick near the bottom of the ingot. The primary blowholes are slightly larger than in the 58-in. ingot and do not form a double zone. The primary-blowhole zone disappears about 62 in. from the butt, tending to merge into the secondary-blowhole zone. The secondary blowholes are smaller than in the 58-in. ingot. The distance from the surface is approximately  $4\frac{7}{8}$  inches.

#### *Experiment G. Normal and Late Capping of Rimmed Ingots*

1. Furnace practice. An addition of spiegel was made to the bath 27 min. before tapping. The bath and slag analyses before the spiegel was added were as follows: C, 0.060 per cent; Mn, 0.10; FeO, 22.2. Ferro-manganese and 45 lb. of aluminum were added to the ladle.

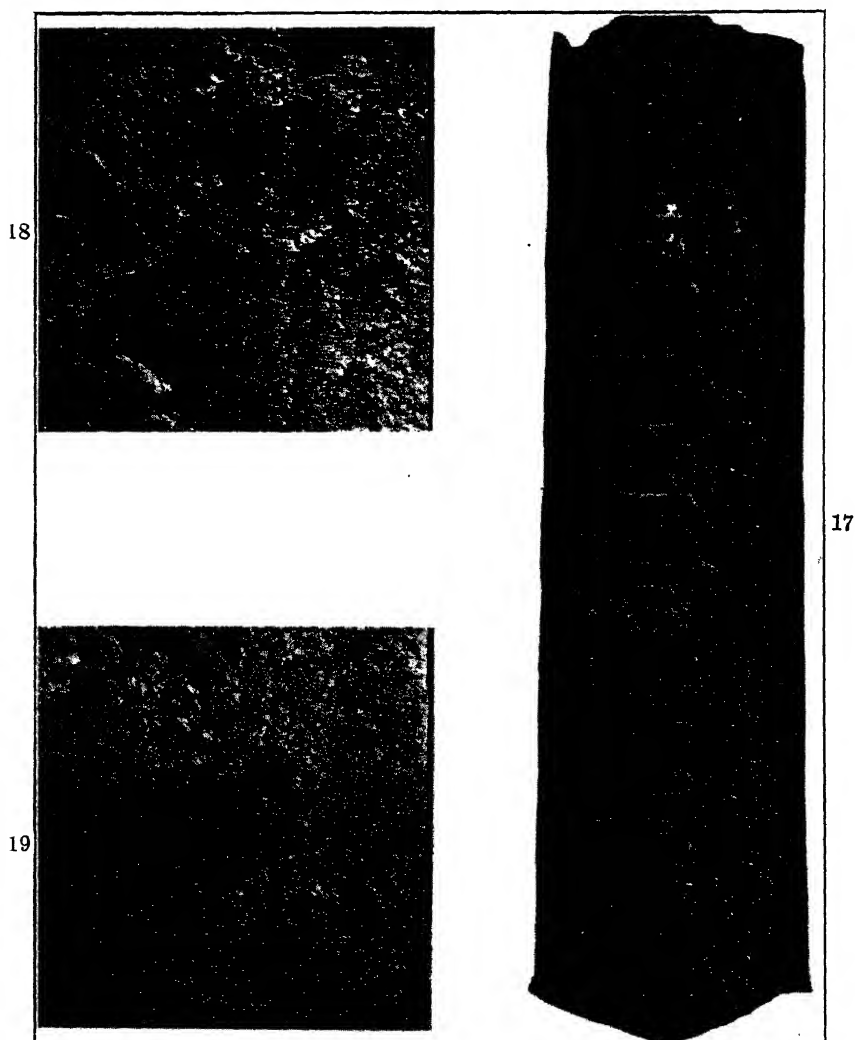
2. Pouring practice. Molds were 24 by 43 in. Hot. Tar on stools. Poured 66 in. high. Eleven ounces of aluminum was fed to each ingot as it was poured. The metal was foamy and jumpy during pouring and dropped 2 to 3 in. after topping off. A strong rimming action developed until a 1-in. rim was formed. The action then subsided and the level dropped 2 in. The ingots rimmed in from this point with a mild action.

Normal capping practice. The fifth ingot was capped at the usual time, when a rectangle of metal about 10 in. wide was still liquid, and before the ingot had started to pyramid. The time from topping off to capping for this ingot was 20 minutes.

Late capping practice. The sixth ingot was allowed to pyramid and erupt before capping. Water was used on the top to prevent further eruptions after the cap was put on. The time from topping off to cap-

ping for this ingot was 36 minutes. Temperature, 2910° F. Clean ladle.

3. Ladle analysis: C, 0.09 per cent; Mn, 0.40; P, 0.008; S, 0.027.



FIGS. 17-19.—EXPERIMENT F. LONG RIMMED INGOT.

Fig. 17. Cross-sectional structure of ingot.

Fig. 18. Enlargement of Fig. 17 showing one side midway between top and bottom

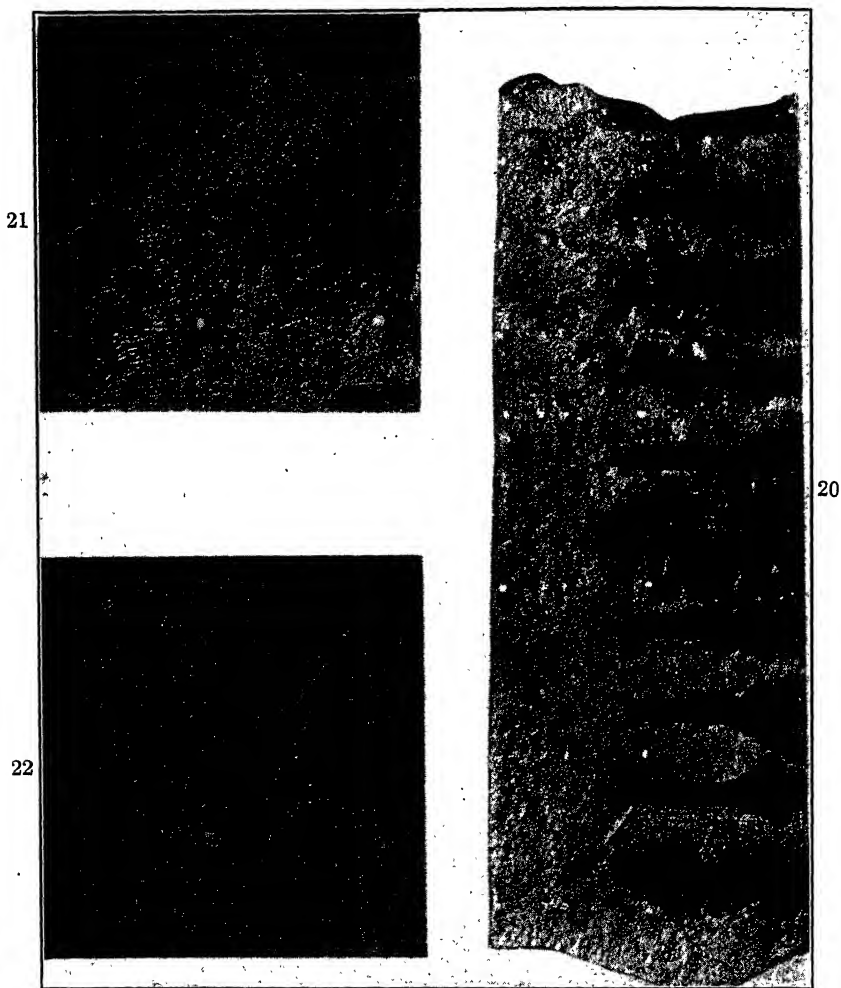
Fig. 19. Enlargement of Fig. 17 showing bottom corner.

4. Ingot structure. The normal and late capped ingots, which were the fifth and sixth ingots poured, were split in half along the 43-in. side.

The structure of the normally capped ingot is shown in Figs. 20 to 22. The skin is  $\frac{5}{16}$  to  $\frac{7}{16}$  in. thick near the bottom of the ingot. The primary blowholes are of medium size. The primary-blowhole zone



disappears about 42 in. from the butt. The secondary-blowhole zone consists of medium sized blowholes. This zone is approximately  $4\frac{7}{8}$  in. from the surface.



FIGS. 20-22.—EXPERIMENT G. RIMMED INGOT, CAPPED NORMALLY.

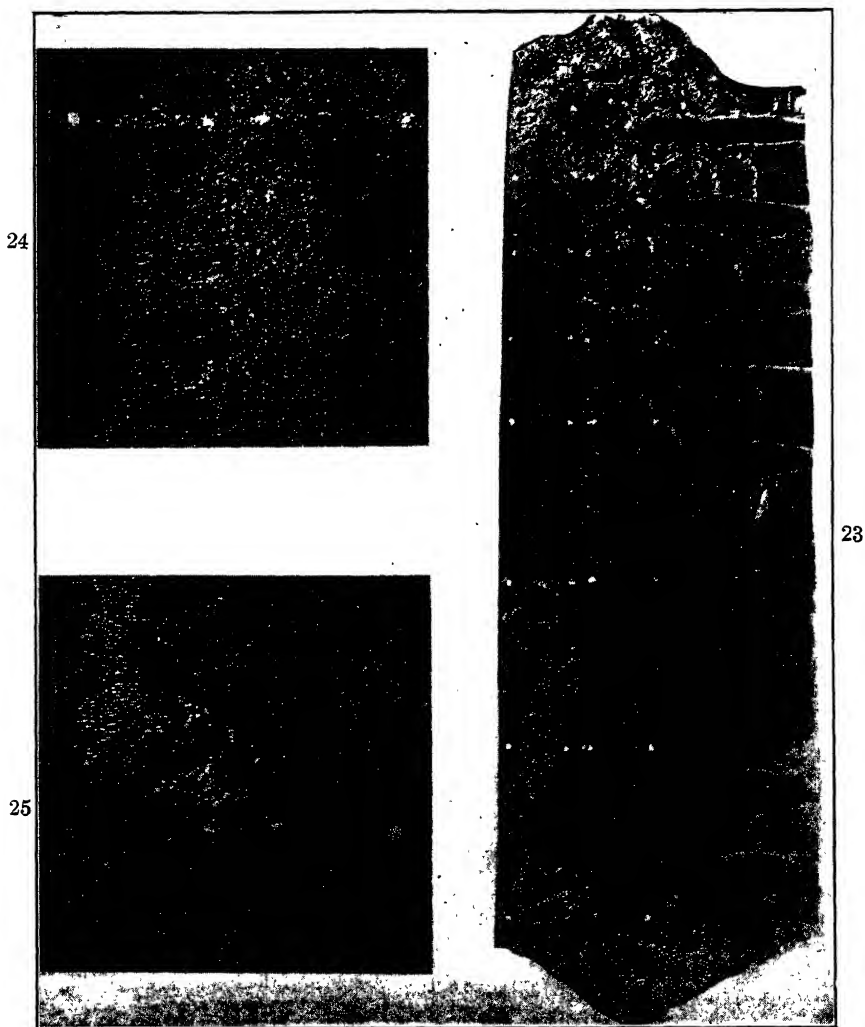
Fig. 20. Cross-sectional structure of ingot.

Fig. 21. Enlargement of Fig. 20 showing one side midway between top and bottom.

Fig. 22. Enlargement of Fig. 20 showing bottom corner.

The structures of the ingot that was capped late are shown in Figs. 23 to 25. The skin is  $\frac{5}{16}$  to  $\frac{3}{8}$  in. thick near the bottom of the ingot. The primary blowholes are of medium size, but slightly larger than in the normally capped ingot. The primary-blowhole zone disappears about 42 in. from the butt. The secondary-blowhole zone

consists of medium to large-sized blowholes, forming a double line in the lower quarter of the ingot. This zone is approximately 6 in. from the surface.



FIGS. 23-25.—EXPERIMENT G. RIMMED INGOT, CAPPED LATE.

Fig. 23. Cross-sectional structure of ingot.

Fig. 24. Enlargement of Fig. 23 showing one side midway between top and bottom.

Fig. 25. Enlargement of Fig. 23 showing bottom corner.

#### *Experiment H. Etched Sections of Bars Showing Effect of Rimming Time*

The object of this experiment was to determine the relation between the rimming time and the width of the rim. A low-carbon rimmed heat,

which was to be rolled into sheet bar, was used for the experiment. An addition of aluminum was made to the tops of the ingots at times varying from  $2\frac{1}{2}$  to 8 min. after finish of pour. Prior to killing with these aluminum additions, the steel had a strong rimming action with a drop of

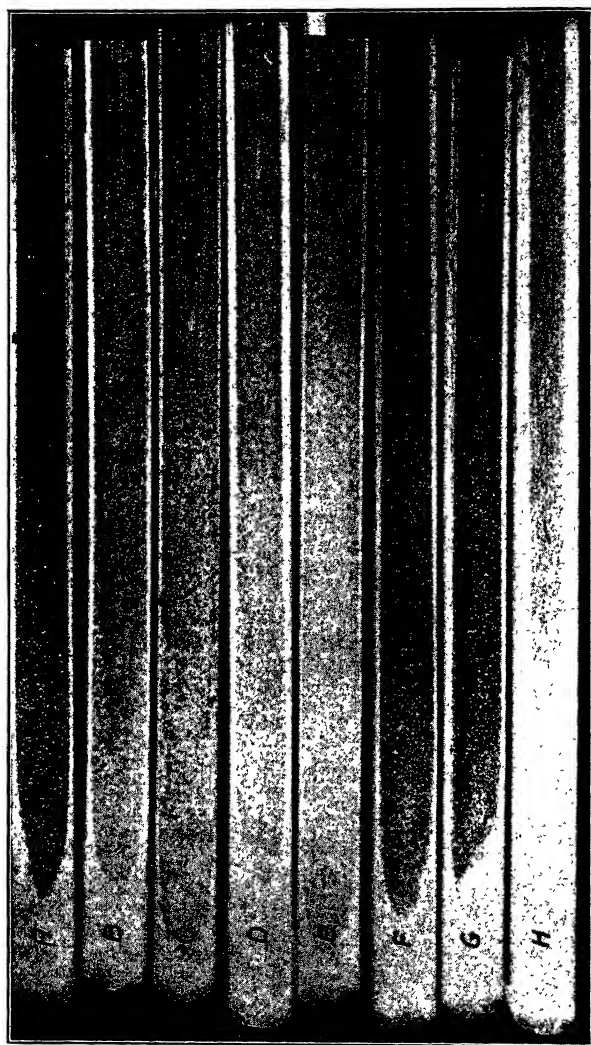


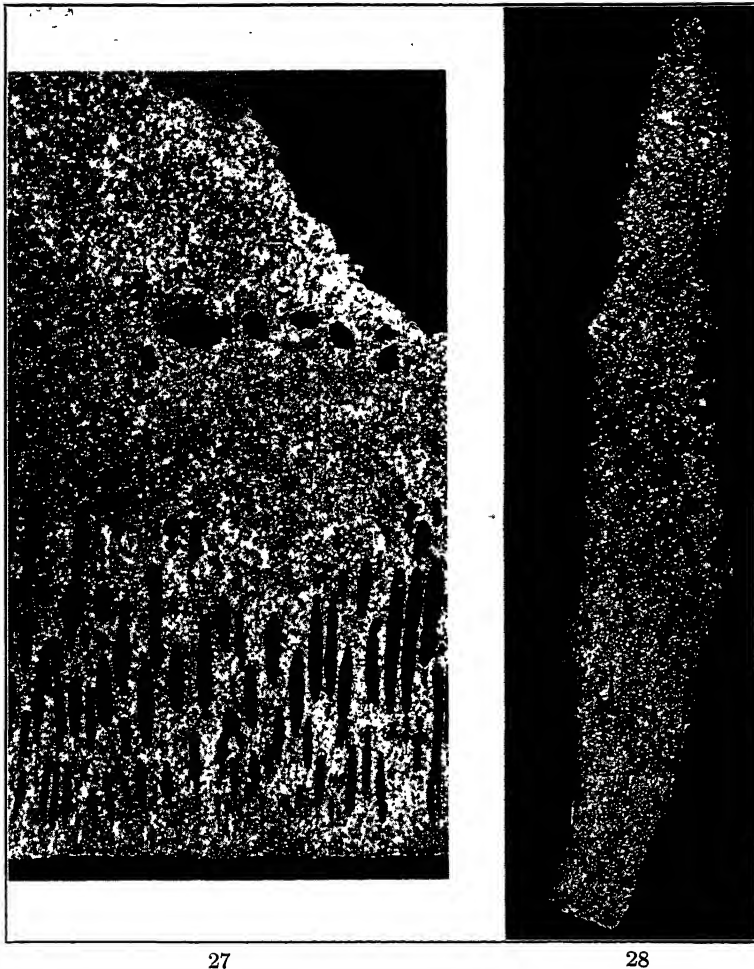
FIG. 26.—EXPERIMENT H. DEEP-ETCHED SECTIONS OF SHEET BARS NEAR TOPS OF INGOTS, SHOWING EFFECT OF RIMMING TIME.

- Test A. 12 lb. of shot aluminum added 6 min. after finish of pour.  
 B. 10 lb. of stick aluminum added 6 min. after finish of pour.  
 C. 10 lb. of stick aluminum added  $2\frac{1}{2}$  min. after finish of pour.  
 D. 10 lb. of stick aluminum added 8 min. after finish of pour.  
 E. 5 lb. of stick aluminum added 4 min. after finish of pour.  
 F. 5 lb. of stick aluminum added 6 min. after finish of pour.  
 G. 5 lb. of stick aluminum added 8 min. after finish of pour.  
 H. No aluminum addition. Ingot rimmed and capped.

4 in. and a 3-in. rise. The ingots that were rimmed and capped normally had flat tops; those killed were flat immediately after the addition, then puffed up 2 to 4 inches.

Fig. 26 shows deep-etch tests on one-half of a cross section near the tops of the ingots. The bar from the rimmed and capped ingot shown in test H has the usual light outer zone and dark center associated with

the low-carbon rim zone and segregated core of the original ingot structure. In the killed ingots the thickness of the rim zone decreases with decreasing rimming time, which indicates that the rim zone is formed only



FIGS. 27-28.—ETCHED SECTIONS OF ZONES OF PRIMARY AND SECONDARY BLOWHOLES.  
Fig. 27. Low-carbon rimmed ingot with large blowholes.  
Fig. 28. Low-carbon rimmed ingot with small blowholes.

while the ingot is actually rimming, and that after capping the core type of structure is formed.

#### *Experiment I. Primary and Secondary Blowhole Zones*

In the course of the experiments on splitting ingots we have occasionally been able to break off pieces that could be prepared for etching. Two of these pieces are shown in Figs. 27 and 28. Fig. 27 is an etched

section of an ingot 22 by 24 by 75 in., of low-carbon rimmed steel, which shows parts of the zones of primary and secondary blowholes, about 25 in. from the butt. The skin is from  $\frac{1}{4}$  to  $\frac{5}{16}$  in. thick and the secondary-blowhole zone is  $4\frac{3}{8}$  in. from the surface. This is a good example of a medium thick skin and large primary and secondary blowholes. Fig. 28 is an etched section of an ingot 24 by 43 by 73 in., of low-carbon rimmed steel, which shows parts of the zones of primary and secondary blowholes about 20 in. from the butt. The skin is about  $\frac{1}{2}$  in. thick and the secondary-blowhole zone is 5 in. from the surface. This is a good example of a thick skin and very small primary and secondary blowholes.

### SOLIDIFICATION AND FORMATION OF BLOWHOLES

The information available on the reactions that occur, the amounts of gas that are formed, and the solubility of the gases in the liquid and solid phases of rimmed ingots is still far from complete. Consequently it is difficult to explain all of the phenomena associated with the solidification and formation of blowholes. In the following discussion, however, an attempt has been made to give a general explanation of these phenomena.

The first metal to solidify when the liquid steel comes in contact with the mold walls forms equiaxed crystals, as a result of the rapid solidification. As the solidification continues the crystallization changes to a columnar dendritic type, which persists during the rimming period and the formation of the rim zone. Selective crystallization occurs with both kinds of crystals, but to a greater degree in the columnar dendritic type. This results in the solid phase being lower in carbon, phosphorus, sulphur and oxides than the original melt, with the rejection of these components to the adjacent liquid phase.

Carbon monoxide is also formed at the boundary of the solid phase, as a result of the reaction  $C + FeO \rightleftharpoons CO + Fe$ . It is also probable that hydrogen is evolved at this point, as a result of the lower solubility of this gas in the solid phase. These gases form at the boundary of the solidification zone and between the branches of the dendrites. The escape of the evolved gas from between the branches of the dendrites sweeps away the impure liquid adjacent to the solidifying metal. The rising of this gas along the solid-liquid interface and its escape at the top of the ingot causes the rolling action of the liquid metal at the surface, which is so characteristic of this type of steel and from which it gets its name of "rimming" steel. This rolling action of the liquid metal at the top keeps the metal from freezing over.

Some of the gas is entrapped, permanently or temporarily, between the branches of the dendrites, displacing the liquid. A rim-zone structure in which the gas has remained and formed primary blowholes consists of a solid phase with less carbon, manganese and phosphorus than the remainder of the ingot, since the liquid between the dendrite branches

is displaced by the gas. The portion of the rim zone that is free from primary blowholes is also low in the elements mentioned above, however, which would indicate that gas had formed between the dendrite branches during the solidification, which either escaped or was reabsorbed, probably the former. In either case, the void would be filled with metal from the liquid phase in the body of the ingot, which would be relatively purer than the impure metal it replaced.

The type of solidification forming the rim zone ceases when the rimming action stops. This may be accomplished artificially by placing a cap on the top of the ingot or adding aluminum to the liquid phase. It will also occur naturally, however, if the ingot is allowed to rim, for when the temperature is low enough the gas evolution decreases until the top freezes over.

The secondary-blowhole zone occurs at the boundary of the rim zone, at the point where the rimming action stops, and presumably is formed from the gas along the face of the solidifying metal that is trapped when the ingot is capped. There is also a higher concentration of carbon, phosphorus, sulphur and oxides at the solid-liquid interface, which will tend to persist in the secondary-blowhole zone.

After the ingot is capped the core zone solidifies, with the formation of equiaxed rather than dendritic crystals. During the solidification of this zone, the temperature is close to the freezing point, and crystallization probably occurs to a certain extent throughout the liquid. The usual type of segregation, however, is found in this zone, and the concentration of carbon, phosphorus and sulphur increases toward the middle and top of the core zone. When the solidification is completed, the top of the core zone is porous and does not resemble the type of pipe found in killed steel. Probably this can be attributed to the fact that gas evolved during the solidification of the core zone collects in the mushy metal under the cap, and prevents the formation of a true contraction pipe. Rimmed steel does not have true pipe characteristic of killed steel, since the volumetric shrinkage resulting from falling temperature in the liquid state and phase change contraction is largely offset by the space occupied by entrapped gas, or blowholes.

#### EFFECT OF FURNACE AND POURING PRACTICE ON STRUCTURE

Many variables in the furnace and pouring practice affect the ingot structure. The effect of some of the variables, such as the relation between the rimming time and the depth of the rim zone, are fairly definite. The effect of others, such as the relation between the iron oxide in the slag and the type of primary-blowhole zone, is indirect, and may be offset by other variables, so that it is often obscured in individual heats. The effect of variables of this class can only be determined by studying a large number of heats and making corrections for the other

variables. In the following discussion variables of both classes have been considered and only a few can be demonstrated by reference to the experiments described earlier in this paper.

The principal variables affecting the thickness of the skin are the mold temperature, steel temperature and rate of pouring. The thickness of the skin is decreased if the mold temperature is too high (over 700° F.) or if the mold is too cold, particularly if the surface is damp or rusty. The thickness decreases with increasing steel temperature and increasing pouring rate. In general, satisfactory skin thickness is associated with the type of rimming action that begins while the ingot is being poured and continues vigorously with no rise, and preferably some drop, in the level of the metal after the ingot is topped off. Examples of thin-skinned and thick-skinned ingots are given in experiments D and E (Figs. 8 to 13).

The size and distribution of the primary blowholes are affected primarily by the iron oxide in the slag, the type and amount of deoxidizers used in the ladle and molds, the temperature of the steel, the ingot dimensions, the height of pour, and the composition of the steel. A low content of iron oxide in the slag is usually associated with a slow evolution of gas and unsatisfactory rimming action—the gas not being ejected readily from between the dendrite branches and not rising freely along the wall of solidifying metal. This type of rimming action results in an increase in the diameter and length of the blowholes, and usually they begin forming closer to the surface, thus decreasing the thickness of the skin. The effect of deoxidizers is also associated with gas evolution, and the use of too great an amount, or of types such as silicon, causes a condition similar to that resulting from too low a content of iron oxide. Excessively high steel temperature results in the formation of blowholes nearer the surface, reducing the thickness of the skin. The mold dimensions, both with respect to the total area of the cross section and the ratio of the two dimensions, have an effect on the rimming action and the type of primary blowholes. The height of pour has a definite effect on the size and height of the primary blowholes, as shown in experiment F. The effect of steel composition is demonstrated by the improvement that occurs in the type of primary blowholes in a low-carbon steel as compared to a high-carbon steel, and by ingot iron that is very low in carbon and manganese and is entirely free from primary blowholes.

The position and characteristics of the secondary blowholes are affected by the iron oxide in the slag, the pouring temperature, the rate of solidification and rimming time, and the sulphur in the steel. A high iron oxide content of the slag and high pouring temperature are associated with the rate of solidification and rimming time, and act to produce deeper seated secondary blowholes with a higher concentration of impurities, which tends to prevent the blowholes from welding when the ingot is rolled. High sulphur in the steel is associated with this same condition,

as a higher concentration of sulphur occurs adjacent to the secondary blowholes. Examples showing the effect of rimming time on the depth of the secondary blowholes are shown in experiments G and H.

#### ACKNOWLEDGMENTS

The authors express their appreciation to the Inland Steel Co. for permission to use the experimental data and results submitted in this paper. They are also indebted to Messrs. H. B. Hubbard and A. P. Miller, of the Open Hearth Department, and Messrs. H. R. Boatman, G. L. Plimpton and K. L. Kerschbaum, of the Metallurgical Department, for their assistance in conducting the experiments and compiling the data.

#### DISCUSSION

[See also page 349]

(*L. F. Reinartz presiding*)

L. F. REINARTZ,\* Middletown, Ohio.—The question of quality in a steel ingot is relative. A man that has been making killed-steel ingots when he sees a picture of a rimmed-steel ingot thinks it is very poor steel. In 1912, Dr. Cushman came to Armco. He had never seen the internal structure of any kind of ingot. We split some ingots. He took one look at the blowholes in the rimmed-steel ingot and went to our president and said, "I do not want to have anything to do with the gang that made that kind of steel." But rimming steel has proved most satisfactory so far for low-carbon sheet and strip steel. The metallurgist and the operator must play between deep-seated blowholes or blowholes too close to the surface, and he has to hit a happy medium.

E. GATHMANN,† Baltimore, Md.—What was the mold temperature? We have found that when molds are quite cold there are very many skin blowholes, much closer to surface than if the mold is fairly warm, say, 250° F. We found that to be the best temperature of the mold for producing deep-seated blowholes.

T. S. WASHBURN.—I do not agree with that entirely. I think a cold, damp mold is likely to give a thin skin, but a cool mold up through to a hot mold probably gives the best skin, and then thin skin occurs again with a very hot mold. I would estimate this temperature to be around 700° or 800°.

MEMBER.—What is the effective cross section?

T. S. WASHBURN.—I think there is a relation between the length and the cross section; that is, the higher the ingot, the greater should be the cross section. There also seems to be some merit in a rectangular mold; which has one side narrower than the other. This type seems to develop a better rolling and rimming action.

F. A. KING,‡ Weirton, W. Va.—I think the cold mold, if it is cold, will have more or less moisture in it, and so you have to have a little warmth to keep it free of the moisture.

T. S. WASHBURN.—The cold mold that is dry will not give much trouble.

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\* Works Manager, American Rolling Mill Co.

† President, Gathmann Engineering Co.

‡ Weirton Steel Co.



F. A. KING.—No, I do not think so, but it is pretty hard to get one that is cold and dry.

T. S. WASHBURN.—In the cold mold there is a violent evolution of the gases and the formation of blowholes takes place quickly, because it freezes more quickly and surrounds that part of the steel. There must be more moisture in a cold mold than in a warm one; I mean one at from 200° to 300°.

C. H. HERTY, JR.,\* Bethlehem, Pa.—It seems to me that the point of the discussion of the cold mold is more that it is impossible to get a dry mold. Every cold mold I know of had moisture coming out after the ingot was poured. It is probably the water vapor coming out that gives the skin blowholes.

Just beyond the primary blowhole zone, there is a steel relatively free from blowholes. Do you know why you get that intermediate area or zone that is free from blowholes?

T. S. WASHBURN.—I should say it is associated with the gas formation with respect to the manner in which the gases evolve and rise along the zone of solidification. In fact, sometimes after the skin is formed primary blowholes will develop, which will tend to be suppressed later and then start in again. In other words, there may be two rows of primary blowholes. The explanation may be that there is developed an evolution of gas at one period that tends to free itself and not be entrapped in the form of primary blowholes; and as the gas evolution changes later in the rimming, blowholes begin to be formed again.

L. F. REINARTZ.—Have you noticed that when you split these ingots you get a series of lines across the primary blowholes, as though the gas came off in surges? That structure seems to be developed in a great many ingots. Instead of having a perfect pipe there is a series of bubbles running all the way along on the ingot, as though the gas had a way of building up enough pressure to let go, and yet not enough volume in the gas to be released, so that a series of bubbles is formed.

J. H. NEAD.—I have frequently noticed the same thing, but I would not say it was a series of bubbles. These parallel lines do occur in the primary blowhole zone, but the blowholes seem to be continuous through those lines. I think that what we need is a thorough investigation of the nature and the amount of gas evolved during ingot solidification. That has been attempted a number of times, but never, so far as I know, been done satisfactorily, and there has never been anything published on it that is really reliable.

Such information, I think, would lead to a clearer understanding of the mechanism of the solidification of rimmed steel.

L. F. REINARTZ.—The British Iron and Steel Institute has done much work on the heterogeneity of rimmed-steel ingots. Its writers have theories as to the cause of blowholes but they have not come to any definite conclusions as to the formation of these gases and how these blowholes are formed.

C. H. HERTY, JR.—There appear to be regular lines of freezing on the walls of the blowholes, indicating that the bubbles come off in surges rather than at random. In cooperation with the M.I.T. School of Chemical Engineering Practice, we have been doing work on gas evolution. In measuring the gas evolved we get these definite surges during the period of primary blowhole formation. And so it is not a question of a bubble coming off as soon as it is formed, but of a bubble having to get up to a certain size.

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\* Research Engineer, Bethlehem Steel Co.

L. F. REINARTZ.—What effect has the thickness of the mold wall on the line of secondary blowholes? It seemed to me that the secondary line of blowholes is determined more by the thickness of the mold wall than by the height of the ingot.

T. S. WASHBURN.—We have made no experiments to correlate those two variables, and yet I would be inclined to disagree. I think it is determined more by the dimensions and weight of the ingot than by the thickness of the mold wall. Our theory is that the secondary line of blowholes is formed when the ingot is capped and the evolution of the gases ceases, and consequently its position is governed by the rate of solidification and the length of time the ingot rims.

B. M. LARSEN,\* Kearny, N. J.—No logical explanation occurs to me for the wavy, vertical line structure in the rim zone mentioned by Dr. Herty, but the existence of two blowhole zones with solid metal between can probably be explained briefly as follows, although a complete explanation would require more time than is available here in discussion: The so-called "skinholes" in the ingot, which form in the rim zone near the surface, are due to gas bubbles formed in the residual liquid and trapped between dendrites growing into the liquid metal at right angles to the mold wall. The reason the bubbles are trapped is essentially the rapid rate of freezing *relative to* the violence of the "rimming action" or stirring in the liquid, especially near the bottom of the ingot. As freezing continues, the rate of growth of crystals inward decreases and the stirring action probably tends to increase, so that these bubbles begin to be swept upward and out of the metal instead of being trapped between dendrites, and the inner portion of the rim zone will usually be solid. When rimming is stopped by the top freezing over or by capping, we then, of course, get the second zone of larger, irregularly shaped blowholes near the transition between "rim" and "core" zones. The whole process is controlled by the balance between the factors of rate of solidification, hydrostatic pressure (i.e., height of metal in the mold) and the rate of gas-bubble formation (i.e., the concentrations of C and FeO in the metal).

H. D. HIBBARD,† Plainfield, N. J. (written discussion).—This is an interesting addition to the literature of rimmed steel, but one might wish for fuller details, particularly of the furnace practice. To have the full story of any steel one must start not later than at the blast furnace, or at least with the crude iron used in making the steel. The different kinds of rimmed steel made by different plants call for minute description of details. No two practices are alike in every particular.

The present writer has had no experience with such large rimmed-steel ingots as are described in the paper and casting conditions are important. It is important whether rimmed steel is to be top-cast or bottom-cast. Each method requires appropriate furnace treatment. Generally speaking, it is easier to get a good rimming effect if the steel is bottom-cast, as the rate of cooling in the mold, which sets free the gases of effervescence, is then more rapid. For top-casting the bath metal needs to be more strongly oxidized, so as to be more gassy. All the steel mentioned in the paper was apparently top-cast.

Blowing ingots apart by dynamite may show up the internal structure to the eye, but a planed or sawed surface photographs better.

What the authors call primary and secondary blowholes the present writer has called skinholes and intermediate gasholes, as indicating their location in the ingot. Skinholes are formed chiefly by hydrogen and intermediate chiefly by carbon monoxide.

The statement on page 379 that "rimming" results from the evolution of gas seems to be inaccurate. The rim is the top of the frozen shell of the ingot. The evolution

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\* U. S. Steel Corporation, Research Laboratory.

† Consulting Engineer.

of gas keeps the top of the still liquid steel "open," not allowing it to freeze until near the end of solidification.

The addition of the spiegel made 20 to 25 min. before tapping seems to the writer to be not needed in view of the high manganese then in the bath metal. Such addition would tend to quiet the boil when more boil was needed rather than less. A little crude by augmenting boil would be better. The low carbon in the metal, indicating considerable if not ample oxygen present, was a saving condition.

The great requirement in making rimmed steel is to have a solid skin at least  $\frac{1}{2}$  in. thick (1 in. is better) form in the ingot before the skinholes start to form. That requires that the hydrogen content of the bath metal is not excessive and that depends, in the writer's opinion largely on three things: (1) that in the crude iron of the charge, (2) water vapor in the melting chamber, and (3) the quantity and vigor of boil of the bath. The first two put it in, the third expels it.

The great point in making rimmed steel is to have, particularly at tapping, a proper temperature of the bath, which will favor a proper evolution of gas in the mold. It should be such as to admit of clean teeming, with perhaps an incipient skull left in the ladle.

T. S. WASHBURN AND J. H. NEAD (written discussion).—The authors agree with Mr. Larsen's discussion, which summarizes satisfactorily the phenomena associated with solidification and gas evolution in accordance with the data at present available. His general theoretical explanation, however, emphasizes the desirability for more accurate information with respect to the solubility of carbon monoxide, hydrogen and nitrogen under the conditions present in rimming steel, both in the bath before tapping and in the two phases at the liquid-solid interface during solidification. Only when such information is available will we be able to progress beyond the indeterminate explanation of the rimming phenomena to which we are limited at present.

We agree with Mr. Hibbard that it would be desirable to have the complete history of a heat of rimmed steel, but we are inclined to believe that it is not necessary to attempt to correlate the quality with the blast-furnace practice and iron analysis. The quality of the steel undoubtedly is influenced by the iron, but only in so far as it effects the type of melt obtained and the analysis of the finishing slag, and if the record of a heat that is being studied includes this melt and slag information it is not necessary to include data with respect to the iron. Mr. Hibbard's comments in regard to the primary blowholes being formed by hydrogen are interesting and we regret that we have no information to substantiate the point. We do not agree with his interpretation of the effect of the spiegel addition. This addition does not tend to quiet the boil, as the bath is more highly oxidized 30 min. after the spiegel addition than it is before the addition. In general, the effect of the spiegel addition made to this type of steel 25 to 30 min. before tapping is to equalize and raise the temperature of the bath, increase the fluidity of the slag and slightly increase the oxidation of the bath at tapping time.

# Some Factors Influencing Segregation and Solidification in Steel Ingots

By LEON H. NELSON\*

(New York Meeting, February, 1937)

SEVERAL factors which affect the segregation and solidification of killed hot-topped steel ingots are: (1) pouring temperature, (2) volume in the hot top, (3) taper in the ingot, (4) pouring rate by varying the nozzle size, (5) segregation of several elements, (6) moving ingots before completely solidified.

In most of this discussion, segregation will be measured in terms of carbon variation only. All the data given are results on S.A.E. 1040 analysis of fully killed steel direct-poured in hot-topped molds giving 20-in. square ingots. Thus the variables of analysis and ingot size and contour are eliminated. Segregation results are all on the rolled-bloom size, not on the ingot itself. They are results from plant-control work and not results of special research on ingot segregation.

## POURING TEMPERATURE

The temperature (or, more correctly, the amount of superheat above the liquidus-solidus) of the steel entering the ingot is, of course, one of the most important factors influencing segregation and solidification. Table 1 gives the average segregation of a number of heats of S.A.E. 1040 steel with normal pouring temperatures of 2775° to 2825° F. The table also gives some data on segregation in hot heats (pouring temperature 2840° to 2870° F.) and in cold heats with some skull (poured at 2725° to 2760° F.).

The results in Table 1 are on steel ingots with 20-in. square cross section and 60 in. long to the hot top. The ingot weighs 7100 lb. and the hot top contains 14.3 per cent of the total ingot volume and 11.2 per cent of the total ingot weight. The results are from drillings after rolling the ingots to bloom size. Segregation results obtained on the bloom are probably not as great as they would be in the ingot itself, since heating the ingots for rolling can perhaps cause some migration of carbon from regions of high and low carbon to those of average carbon content.

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Manuscript received at the office of the Institute Dec. 1, 1936.

\* Open Hearth Metallurgist, Republic Steel Corporation, Buffalo, N. Y.

"Positive segregation" indicates higher than ladle analysis and "negative segregation" indicates lower than ladle analysis.

TABLE 1.—*Effect of Pouring Temperatures on Carbon Segregation in S.A.E. 1040 Ingots<sup>a</sup>*

Distance from Butt of Ingot, Per Cent of Ingot Weight	Hot Heats			Normal Heats			Cold Heats		
	Edge	Halfway	Center	Edge	Halfway	Center	Edge	Halfway	Center
88		+0.037	+0.220	+0.004	+0.039	+0.127			
86		+0.031	+0.085		+0.033	+0.060			
84		+0.028	+0.048		+0.027	+0.050		+0.056	+0.072
82					+0.026	+0.036			
80					+0.024	+0.030			
78					+0.019	+0.027			
70					+0.016	+0.019			
45		+0.018	-0.008	0.000	+0.004	-0.020		-0.018	-0.042
5		+0.005	0.000	-0.002	-0.009	-0.012		-0.012	-0.016

<sup>a</sup> Plus sign indicates positive segregation, above ladle carbon content.

Minus sign indicates negative segregation, below ladle carbon content.

The data of Table 1 lead to the following comments on the effect of pouring temperature on carbon segregation in 20-in. square ingots of S.A.E. 1040 steel.

1. The portion of the ingot near the surface will analyze very close to the ladle analysis from top to butt of the ingot. The interior, however, will show varying degrees of segregation, positive segregation near the top and negative segregation in the lower portions.

2. At 80 per cent bloom yield, heats with normal pouring temperatures will show about 0.045 per cent carbon segregation from top to butt along the central axis, which is the region of greatest segregation.

3. Hot heats give more positive segregation at the center of the cross section near the top of the ingot; they also tend to give less negative segregation in the center in the lower portion of the ingot.

4. Cold heats show appreciably more segregation from top to butt than normal heats. The cold heats have more positive segregation at the top and usually more negative segregation at the butt of the ingot.

Fig. 1 shows the regions of over about 0.01 negative segregation and over about 0.01 positive segregation. It must be remembered that these segregation results are on plain carbon steels of about 0.40 carbon, made with a certain deoxidation practice. Alloy steels practically always show less carbon segregation than plain carbon steels of corresponding carbon content. Carbon segregation in plain carbon steel will also vary to some extent with different deoxidation practices.

## VOLUME IN HOT TOP

The writer has compared the segregation in 20-in. square ingots poured in the same molds but with different volumes in the hot top. All ingots had the same kind of hot top, in which the volume was changed by pouring steel to different heights in the hot top itself. The results of Table 2 show the effect of hot-top volume on segregation in the ingot. The ingots with the smallest volume of steel in the hot top (13.0 per cent) gave the greatest amount of segregation. These ingots also tended to pipe enough to give lower bloom or billet yields than ingots with greater volume in the hot top. On the other hand, results indicated no advantage here in using over 14.3 per cent volume in the hot top for this size of ingot.

## TAPER IN INGOT

The writer has recently had the opportunity to compare ingots of practically the same size in cross section and weight but with different amounts of taper. These ingots were 20 in. square by 60 in. long, one ingot having 2-in. taper while the other had 3-in. taper. Table 3 gives the segregation results in the two ingots from a heat that had a small skull, and which, therefore, had a lower pouring tempera-

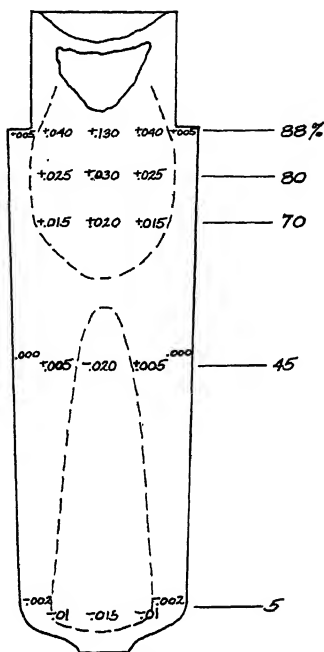


FIG. 1.—REGIONS OF OVER 0.01 POSITIVE AND NEGATIVE SEGREGATION IN A 20-INCH SQUARE INGOT OF S.A.E. 1040 POURED AT NORMAL TEMPERATURE.

TABLE 2.—*Effect of Hot-top Volume on Carbon Segregation in S.A.E. 1040 Ingots*

Distance from Butt of Ingot, Per Cent of Ingot Weight	17.0 Per Cent Volume, 13.3 Per Cent Weight, in Hot Top		15.6 Per Cent Volume, 12.2 Per Cent Weight, in Hot Top		14.3 Per Cent Volume, 11.2 Per Cent Weight, in Hot Top		13.0 Per Cent Volume, 10.2 Per Cent Weight, in Hot Top	
	Halfway	Center	Halfway	Center	Halfway	Center	Halfway	Center
87	Above H.T. junction		+0.037	+0.043	+0.045	+0.059	+0.025	+0.105
85	+0.041	+0.037	+0.041	+0.058	+0.042	+0.046	+0.034	+0.055
83	+0.041	+0.046	+0.040	+0.058	+0.034	+0.042	+0.030	+0.045

ture than normal. These results show somewhat less positive segregation at 78 to 85 per cent distance from the butt on the ingot with the greater

amount of taper. Routine tests on a number of other heats using these ingots also indicated that the ingots with 3-in. taper showed somewhat less segregation than the ingots with 2-in. taper.

TABLE 3.—*Effect of Taper in Ingot on Carbon Segregation in S.A.E. 1040 Steel*

Distance from Butt of Ingot, Per Cent of Ingot Weight	Ingot with 2-in. Taper		Ingot with 3-in. Taper	
	Halfway	Center	Halfway	Center
87	+0.048	+0.048	+0.048	+0.062
85	+0.048	+0.064	+0.044	+0.048
83	+0.044	+0.054	+0.048	+0.040
80	+0.032	+0.064	+0.036	+0.052
78	+0.044	+0.072	+0.040	+0.030
72	+0.036	+0.020	+0.024	+0.040
62	+0.044	+0.014	+0.020	+0.008
51	+0.028	+0.002	+0.016	+0.000
46	+0.016	+0.020	+0.008	+0.026

#### EFFECT OF POURING RATE CAUSED BY VARYING THE NOZZLE SIZE

The carbon segregation in 20-in. square ingots poured through nozzles of three different sizes ( $1\frac{3}{4}$ ,  $1\frac{1}{2}$  and  $1\frac{1}{4}$ -in. diameter) seems not to be appreciably affected by the varying pouring rate. Table 4 gives average segregation results on a number of S.A.E. 1040 heats poured with the three nozzle sizes.

TABLE 4.—*Effect of Pouring Rate on Carbon Segregation in S.A.E. 1040 Ingots<sup>a</sup>*

Distance from Butt of Ingot, Per Cent of Ingot Weight	Ingot Poured	$1\frac{3}{4}$ -in. Nozzle	$1\frac{1}{2}$ -in. Nozzle	$1\frac{1}{4}$ -in. Nozzle
84	First	+0.025	+0.024	+0.029
	Last	+0.026	+0.024	+0.031
45	Middle	+0.014	+0.008	+0.014
	Last	+0.004	+0.003	+0.008
5	First	-0.010	-0.014	-0.009

<sup>a</sup> These segregation results at halfway from edge to center of cross section.

The three nozzle sizes give much difference in pouring rate near the start of pouring. However, the smaller nozzles seem to erode more rapidly, so that after about one-half of the heat is poured, the difference in pouring rate is not great. The average pouring rate for a whole heat is only 15 per cent slower with a  $1\frac{1}{2}$ -in. nozzle than it is with a  $1\frac{3}{4}$ -in. nozzle. The average pouring rate with a  $1\frac{1}{4}$ -in. nozzle is only 25 per cent slower than it is with a  $1\frac{3}{4}$ -in. nozzle. Since the  $1\frac{3}{4}$ -in. nozzle

gives a more uniform pouring rate throughout the pouring of a heat, the writer prefers it to the smaller sized nozzles mentioned.

### SEGREGATION OF SEVERAL ELEMENTS

Most of the commoner elements present in steel will segregate in somewhat the same manner and degree as carbon. Table 5 shows the segregation of carbon, manganese, phosphorus, sulphur and silicon in a single heat of S.A.E. 1040 steel and also the average segregation in several grades of steel.

TABLE 5.—*Segregation of Various Elements in a Heat of S.A.E. 1040 Steel*

Element	Ladle Analysis, Per Cent	Segregation, 85 to 5 Per Cent from Butt	Segregation, Per Cent
Carbon.....	0.43	0.052	12
Manganese.....	0.74	0.06	8
Phosphorus.....	0.025	0.003	12
Sulphur.....	0.030	0.005	16
Silicon.....	0.26	0.01	4

### AVERAGE SEGREGATION IN SEVERAL GRADES OF STEEL

Element	Grade of Steel	Segregation, 85 to 5 Per Cent from Butt	Segregation, Per Cent
Carbon.....	S.A.E. 1040	0.05	12
Manganese.....	S.A.E. 1340	0.15	9
Sulphur.....	S.A.E. 1130	0.025	20
Nickel.....	S.A.E. 2330	0.18	5

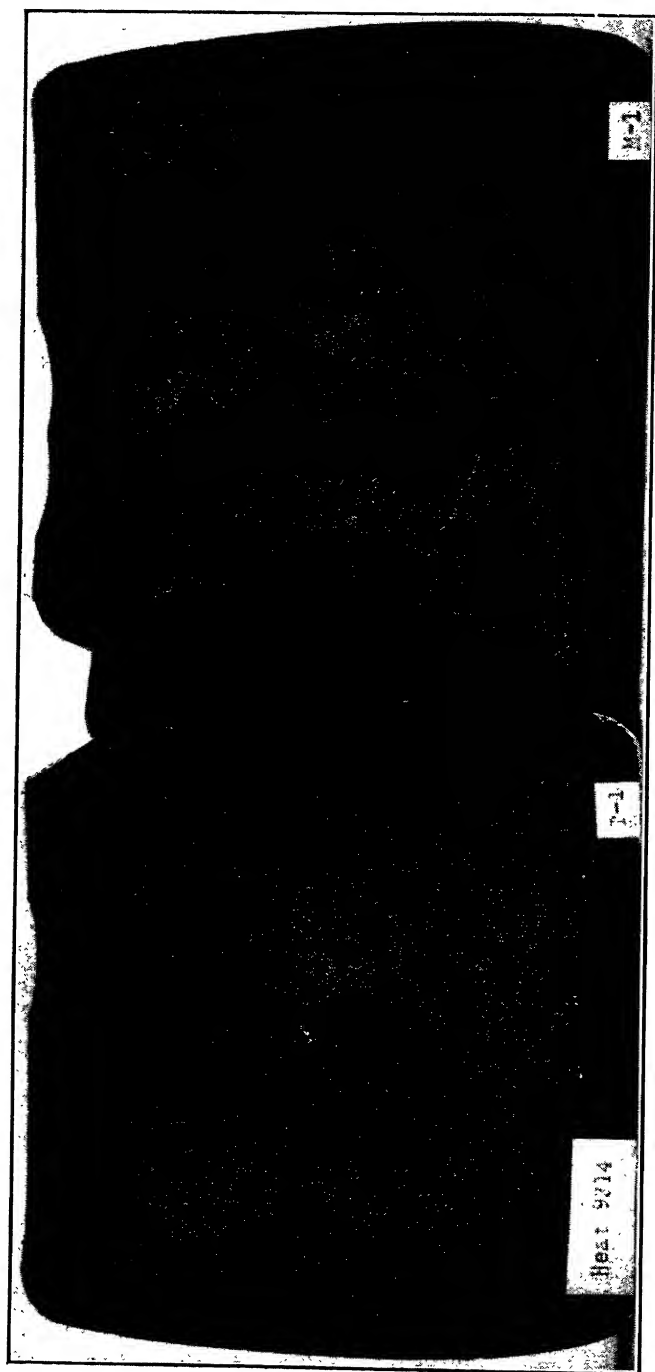
### MOVING INGOTS BEFORE COMPLETELY SOLIDIFIED

The writer has always been a firm believer in holding killed ingots until completely solidified before moving them. This is justified by the uniformly sound steel produced even if it does mean lower temperature of the ingots entering the soaking pits. In an earlier paper<sup>1</sup>, the writer demonstrated that a good working rule for calculating the time of solidification on usual size "big end-up" ingots is as follows: The time of solidification (in minutes) equals the square of half the small cross sectional dimension (in inches) of the top of the ingot. Thus, for an ingot having 20 in. as the shortest dimension at the top, the time for complete solidification will be approximately 100 minutes, or  $T = \left(\frac{20}{2}\right)^2 = 100$ .

Fig. 2 show the macroetch of billet cross sections from a heat of S.A.E. 3140 steel that was moved too soon. The ingots were moved from

<sup>1</sup> L. H. Nelson: Solidification of Steel in Ingot Molds. Presented at convention of Amer. Soc. for Metals, October, 1933.





Top  
Fig. 2.—Unsoundness in billets produced by moving an S.A.E. 3140 ingot not completely solidified.

the pouring platform about 40 min. after pouring; then stripped and charged into the soaking pits about 60 min. after pouring. Note the unsound centers where the steel was still in a mobile state when charged into the soaking pits. Other ingots on the same heat that were held for 90 min. before moving gave perfectly sound billets.

This illustration may seem to be a somewhat exaggerated example, nevertheless it suggests the desirability of keeping killed ingots stationary until they are entirely solidified or else moving them continually during solidification, as is done sometimes.

### SUMMARY

The data presented lead to the following observations concerning the segregation in killed S.A.E. 1040 ingots, 20 in. square:

1. Normal pouring temperatures are best to avoid excessive segregation.

2. The volume of metal in the hot top must be correct to keep segregation at a minimum. Volumes that are too small give segregation and pipe; volumes that are too large mean a waste of steel.

3. The segregation may be influenced by the taper in the mold.

4. The rate of pouring the ingot (within the limits mentioned) does not affect segregation. Excessively fast or excessively slow pouring, however, probably has an influence.

5. It is important that killed ingots should not be moved before they are completely solidified.

In conclusion, the writer wishes to suggest that in determining ways of preventing excessive positive segregation at the top of ingot the experimenter should not neglect to test the segregation and soundness lower down in the ingot. It is the writer's experience that some procedures that reduce positive segregation at the top of the ingots may also increase negative segregation and unsoundness along the central axis near the middle of the ingot.

### ACKNOWLEDGMENT

The writer wishes to thank the management of the Republic Steel Corporation for permission to publish the data presented here.

### DISCUSSION

[See also page 349]

(*L. F. Reinartz presiding*)

E. GATHMANN,\* Baltimore, Md. (written discussion).—Mr. Nelson is to be congratulated on the thoroughness that characterizes his experiments and the excellent manner in which he presents his findings.

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\* President, Gathmann Engineering Co.

The data regarding teeming temperatures, hot-top volumes, percentages of taper, nozzle sizes and the desirability of keeping fully killed steel ingots stationary until completely solidified is in accordance with our experience. However, there are two other factors that should be included to make the picture of solidification and segregation more nearly complete; viz., the effects of mold temperatures at the time of teeming and the cross-sectional contours of the mold chambers.

*Mold Temperature.*—In a jag of 20 to 30 molds, unless due precautions are taken to assure approximate uniformity of temperature, there may frequently be a variation of 100° F. and even as much as 200° F. between the low and high temperatures of the molds. Cold molds—those at atmospheric temperature at the time of teeming (especially in winter)—produce segregation similar to that existing when heats are teemed on the cold side; and excessively hot molds (those used for a heat and then re-used before having cooled sufficiently) give results similar to “hot” heats. This is true even though the molten metal is teemed at what is considered normal or best pouring temperature for the specific type of steel.

*Air Gap and Segregation.*—One of the most important functions of corrugated mold chambers is to delay the formation of an air gap at the primary faces of the ingot, so that there will be a longer period of initial contact of the ingot skin with the mold matrix. This longer initial contact produces a materially thicker equiaxed, chill, crystalline ingot skin and considerably shortens the period of complete solidification of the ingot metal. Mr. Nelson's formula for time of solidification is approximately correct when applied to suitably corrugated ingots. For plane-sided square ingots of 20-in. top cross section and 2-in. taper in a 72-in. length, we have found that approximately 2 hr. is required for complete solidification in car practice and 2½ hr. in pit practice. As the percentage of segregation in fully killed steels is approximately proportional to the time of complete solidification, a suitably corrugated ingot, all other factors being equal, should have about 12 per cent less segregation than a plane-sided contour. Increasing the taper of an ingot, especially in high-carbon and alloy steels, lessens both positive and negative segregation by retarding the formation of the air gap and thus shortening the period of solidification. Our experience is that the taper in a rectangular corrugated mold of 20-in. top cross section for use in car practice should be at least ½ in. per foot of chamber height.

W. J. REAGAN,\* Pittsburgh, Pa.—Has the author done anything about the reason for the taper affecting the segregation? We have a little different type of story on our bottom-cast products, but generally we find the same results.

L. H. NELSON.—I cannot answer that satisfactorily, so I will not try to answer it at all. It is true, though, and I have proved it in several instances, and Mr. Gathmann spoke of expressing taper in inches per foot—that is, of course, the proper way to do. One ingot had 0.4-in. taper per foot, and the other 0.6-in. taper per foot; I think at least a ½-in. taper per foot is desirable.

G. SOLER,† Canton, Ohio.—I believe that Mr. Nelson has adhered to the subject of solidification and effect on segregation without digressing to various other effects of pouring practice that might be considered.

The nozzle has an important function in pouring steel, and one can vary the nozzle diameter in order to produce certain effects. For instance, decreasing the size of the nozzle increases the relative amount of surface area exposed to the air while the steel is traveling from the nozzle to the bottom of the mold.

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\* Edgewater Steel Co.

† Manager, Mill Met. and Research, Timken Roller Bearing Co.

The increase of surface area varies, of course, directly with the radius of the nozzle hole, and the volume with the square of the radius. Consequently, with the small nozzle the steel is cooled more rapidly than with a larger nozzle, and a thick-skinned ingot can be produced. Our experiments have proved these observations to be valid.

We have also experimented with steel poured through a basket or double-pour ladle so that a constant head is maintained; we have used nozzle of different sizes for measuring the rate of build-up or cutout from ingot to ingot. These experiments have been conducted on a large number of heats. In general, we agree with Mr. Nelson that the small nozzle will usually cut out to a greater finished size than a larger nozzle. This, however, can be compensated for by the use of different nozzle materials.

L. F. REINARTZ,\* Middletown, Ohio.—Is it not a fact that the cutting out of the nozzle depends largely on the head of the metal in the ladle?

L. H. NELSON.—Of course, the nozzle cuts more rapidly near the first third of the heat when we still have a pretty fair head of metal. Even then, the rate of cutting on the small-area nozzle is greater than on a  $1\frac{3}{4}$ -in. nozzle. There is a difference of 26 per cent in areas between the  $1\frac{1}{2}$  and  $1\frac{3}{4}$ -in. nozzles when we start, and by the time we finish there is probably only a 10 per cent difference in the area. So a heat being poured with a small nozzle has a more variable pouring rate from one end of the heat to the other than is caused, say, with a  $1\frac{3}{4}$ -in. nozzle. In any event, when there is trouble with a little skull forming around the stopper head, then there is more trouble with the smaller nozzle. There are, of course, certain types of steel that probably demand a smaller nozzle.

A. B. KINZEL,† New York, N. Y.—There is one other factor that has not been particularly stressed. Undoubtedly, the segregation is largely effected by the temperature difference between the solidus and the liquidus; the difference in the behavior of alloy steel and carbon steel is probably illustrative, and we know the difference between steels of the automotive type here mentioned and tool steels, so that this range probably is very important in consideration of the problem of segregation in an ingot, and perhaps more important than many of the other factors mentioned.

F. A. KING,‡ Weirton, W. Va.—I think the smaller nozzle will give a little better ingot in the first 25 per cent heat.

L. F. REINARTZ.—What effect has the "head" of the metal on the cutting out of the nozzle?

F. A. KING.—In the lower carbon range, the temperature of the metal has a great deal to do with the cutting out of the nozzle.

T. S. WASHBURN,§ Indiana Harbor, Ind.—Did you encounter porosity underneath the shoulder of the hot top—that is, a porous condition of the section underneath the inset poured at the top?

L. H. NELSON.—You mean the shoulder between the base of the hot top and the mold. Yes, we sometimes do, but that is generally too high for practical use—that is, for quality steels—and so there is no detriment as far as operation is concerned. Up there is the 86 and 88 per cent yield, and that is not obtainable in good killed steel. That portion of the ingot does tend to be a little porous at times, but not often.

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\* Works Manager, American Rolling Mill Co.

† Chief Metallurgist, Union Carbide and Carbon Research Laboratories, Inc.

‡ Open Hearth Superintendent, Weirton Steel Co.

§ Metallurgist, Inland Steel Co.

L. F. REINARTZ.—We had a very interesting confirmation of what Mr. Nelson reported in regard to the pulling of heats and placing them in the soaking pits too early. During the war we were making 6-in. shells, and a great many slugs were being rejected on account of "woody" centers. We made several investigations with the Government inspectors and found that we were placing the 18 by 20-in. and 20 by 22-in. ingots into the soaking pits about an hour after they were poured. When we lengthened the time before charging the ingots to  $2\frac{1}{2}$  hr. the "woody" sections disappeared and we had fewer rejections.

# Variants Influencing Austenite Grain Size as Determined by Standard Methods

BY R. SCHEMPF\* AND C. L. SHAPIRO†

(New York Meeting, February, 1936)

DURING the past few years, general interest in the steel-producing and steel-consuming industries has been centered on the so-called "inherent characteristics" of steels. While often vaguely described, these characteristics are known to influence the response to heat-treatment and the hardening characteristics of the material.

Although most of the recent papers and discussions have associated the "inherent characteristics" with the austenitic grain size and emphasized the importance of it, comparatively little is known of the variables that may affect the size of the austenite grain.

The work to be described in this paper was carried out during the course of a study on the inherent characteristics of tool steel containing one per cent carbon. The discrepancies encountered in the determination and classification of the austenitic grain size led to an investigation of some of the variants influencing the austenitic grain size as determined by standard methods.

## METHODS OF DETERMINING AUSTENITIC GRAIN SIZE

The present methods used for the determination of the austenitic grain size may briefly be classified in two groups:

1. Etching at room temperature to reveal the austenite grain size prior to cooling.
2. Etching at elevated temperatures, cooling to room temperature, and observing the structural conditions that existed at the temperature from which cooling occurred.

The outstanding methods of the first group are: (1) the McQuaid-Ehn test, (2) optimum rate of cooling, (3) quenching and etching.

*McQuaid-Ehn Test.*—This established and accepted test does not need much elaboration. It consists of pack carburizing at a definite temperature for a standard period of time and slowly cooling in the furnace. The temperature is 1700° F. (925° C.) and the time is 8 hr. The interpretation and evaluation of this test are fairly well defined in the A.S.T.M.

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standardization procedure and standard grain-size chart for the classification of steels, A.S.T.M. Designation E 1933, and does not warrant further discussion at this time.

*Optimum Rate of Cooling.*—This method of determining the austenite grain size necessitates a careful regulation of the cooling rate and should only be resorted to on hypoeutectoid and hypereutectoid steels; that is, on materials that possess an excess constituent, either ferrite or cementite.

Davenport and Bain<sup>1</sup> describe this method of optimum cooling as follows:

*Distinctly Hypereutectoid Steels:* In most cases, particularly with plain carbon steels, it suffices merely to cool the specimen in air after heating substantially according to the schedule contemplated or observed in the commercial operation under consideration. The specimen, which may vary from perhaps a quarter-inch section to a small billet, may be cooled at any moderately slow rate, and about each austenite grain a continuous envelope of carbide will be formed which offers sufficient contrast to the pearlite to make grain size estimation quite feasible.

If the steel contains considerable alloy or if it is only slightly hypereutectoid, it may be necessary to transfer the specimen, after heating and prior to final cooling, to another furnace or bath at a temperature just about  $A_1$  for several minutes to insure the formation of the intergranular carbide network. The ideal cooling rate is then that which will form a black-etching pearlite of finest lamellae; in the larger sections, an oil quench is often effective. In some alloy steels martensite may form, in which case contrast between network and ground mass may be developed either by tempering and etching with alcoholic nitric acid or by etching in boiling sodium picrate solution.

*Moderately Hypoeutectoid Steels:* In many cases in which the volume of proeutectoid ferrite is inherently comparatively small the same general procedure as for hypereutectoid steels may be effectively employed. The network marking out the austenite grain will, in this case, be ferrite and the etching technique is appropriately selected. Likewise if the steel is only slightly hypoeutectoid a brief halt in the cooling at a temperature just above  $A_2$  will aid in forming a more nearly continuous network of contrasting ferrite. When the carbon content of the steel is much lower with respect to the eutectoid composition good results may usually be secured by halting the cooling at a temperature just below  $A_2$  and then cooling rather more rapidly than for eutectoid composition, e.g., by an oil quench; the network is thus rendered more narrow and clean cut.

*Low-Carbon Steels:* A moderately small sample is preferable; it is cooled from an appropriate heating temperature to somewhat below the  $A_2$  temperature where it is held for a few minutes to establish a ferrite network. It is then quenched as rapidly as possible. If not too low in carbon a subsequent tempering will produce a dark etching ground mass, particularly if the boiling sodium picrate solution is used as an etching agent. In some cases, when the carbon content is very low, only the texture of the etched surface serves to mark out the network and considerable patience and experience may be required to estimate the grain size.

*Eutectoid Steels:* With no proeutectoid constituent to form in the grain-boundaries of the austenite, the grain is often obliterated with the transformation, either to pearlite or to martensite, or its tempered products. However, one characteristic of the transformation to fine pearlite serves to mark out the grain boundaries with

<sup>1</sup> E. S. Davenport and E. C. Bain: General Relation Between Grain Size and Hard-  
enability and the Normality of Steels. *Trans. Amer. Soc. Metals* (1934) 20, 879.

remarkable clarity; the transformation invariably begins in the grain boundaries at a number of points acting as nuclei. Accordingly, if the steel is cooled at a rate just less than the critical quenching speed, the microscopic specimen shows clearly where the boundaries of the parent austenite lay. For any eutectoid carbon steel, a specimen of suitable size may be chosen for quenching so that at some point in its section the cooling must have been at the optimum rate. In rare cases of rather high alloy steels this type of demarcation of the grains may have to be secured by cooling the specimens quickly into a lead bath for a determined interval at a temperature of some 100 to 200 degrees Fahrenheit (50 to 100° C.) below the  $A_1$  to permit the desired degree of transformation to fine pearlite to occur, after which the specimen is quenched into water to insure that the remainder of the specimen becomes martensitic.

*Quenching and Etching.*—The procedure of determining the austenitic grain by quenching and etching is really but a modification of the preceding method. Dr. Grossmann and Miss Baeyertz were among the first to bring attention to the fact that the original austenitic grain boundaries may be observed in hardened steel after suitable etching. The procedure consists of quenching and etching in a manner by which the etching reagent will either stain or dissolve the austenitic grain boundaries that existed prior to cooling.

As most of the known methods of determining the austenitic grain size by this means did not give entirely satisfactory results when working with heat-treated high-carbon tool steels, the procedure developed to bring out the parent austenitic grain in the material under consideration consisted of etching in a solution of 1 per cent nitric acid and 1 per cent picric acid from 2 to 5 min., washing in alcohol and drying. To keep the contrast between grain and boundary at a maximum, it was found desirable to wash in alcohol instead of water. Another method, of which the results were very consistent and satisfactory, was to etch for 10 to 20 sec. in a 10 per cent solution of nital (15 c.c. of nitric acid per 100 c.c. of ethyl alcohol), washing in alcohol and drying. This method seemed best in bringing out the austenitic grain in tempered material.

The differential attack of the etching reagents, which developed the required contrast for the examination of the austenitic grain, is illustrated in Figs. 1 to 4. Fig. 5 reveals an enormous austenitic grain (delineated by the cementite boundary) which, when examined at a low magnification, creates the impression of being an agglomeration of a number of small grains.

*Etching at Elevated Temperatures.*—The second classification of determining the austenitic grain size of steels involves the etching of polished specimens at elevated temperatures, using a suitable high-melting-point chloride compound as the etching reagent. The polished specimen is immersed in the molten compound (cadmium chloride) at the desired temperature. After heating for a sufficient length of time, usually 5 to 30 min., this specimen is then water-quenched and washed in alcohol to remove the decomposition product caused by the etching attack. A



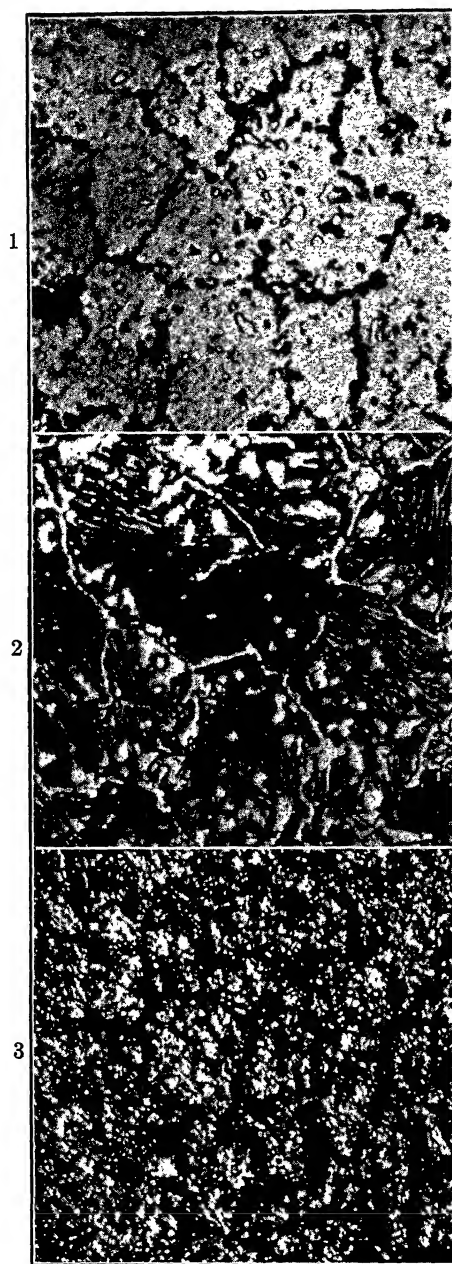


FIG. 1.—AUSTENITIC GRAIN SIZE IN STEEL QUENCHED FROM 1700° F. (925° C.) IN OIL.

Etched 3 minutes in 1 per cent nital-picric acid solution.

FIG. 2.—AUSTENITIC GRAIN DELINEATED IN STEEL ANNEALED FROM 1700° F. (925° C.).

Etched 5 minutes in 1 per cent nital-picric acid solution.

FIG. 3.—AUSTENITIC GRAIN IN STEEL QUENCHED FROM 1700° F. (925° C.) IN WATER.

Etched 5 minutes in 10 per cent nital. All  $\times 1000$ .

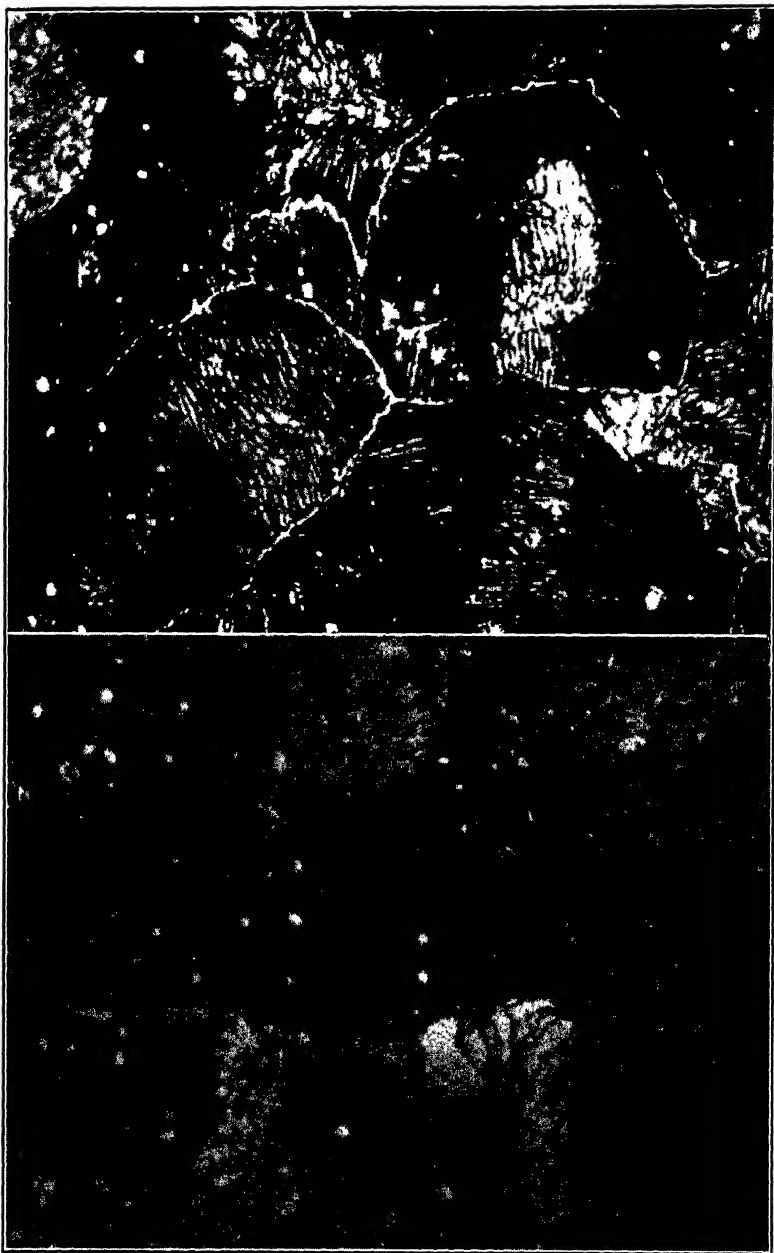


FIG. 4.—AUSTENITIC GRAIN OUTLINED BY CEMENTITIC NETWORK IN STEEL NORMALIZED FROM 1700° F. (925° C.).  $\times 1000$ .

Etched 1 minute in 1 per cent nital-picric acid.

FIG. 5.—STRUCTURAL VARIATIONS IN A VERY COARSE SINGLE GRAIN.  $\times 1000$ .

Etched 1 minute in 1 per cent nital-picric acid.

slight repolishing, which serves to intensify the contrast, then renders the specimen ready for microscopical examination.

The typical austenitic grain-boundary condition that may be obtained in this manner at 1600° F. (870° C.) is shown in Fig. 6.

A careful study and comparison of the austenitic grain size as obtained by the various methods of determination showed the final results to be in

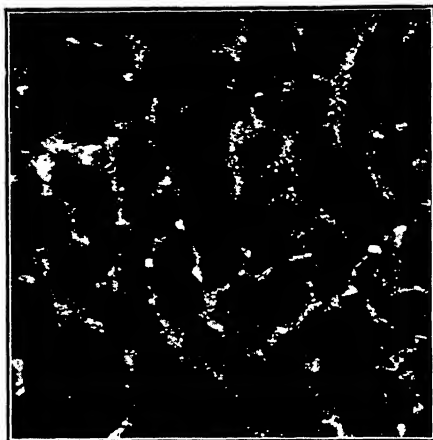


FIG. 6.—AUSTENITIC GRAIN OUTLINED BY ETCHING IN  $\text{CdCl}_2$  AT 1700° F. (925° C.).  $\times 100$ .

Grain boundaries in relief (white); grain depressed (black).

fairly close agreement, with the exception of the McQuaid-Ehn test grain-size ratings, which seemed to be markedly influenced by certain variables.

*Material.*—The material that was used in our efforts to develop the variables that may influence the grain-size ratings as interpreted by the McQuaid-Ehn test method was straight 1.00/1.10 per cent carbon basic electric tool steel. The compositions of the heats most frequently used in this work are given in Table 1.

The so-called "inherent characteristics" of these heats as determined by the now fairly well established P/F test, as developed by Shepherd and described in his various papers, and the slab-hardening test, together with the McQuaid-Ehn grain sizes of these heats, as determined in accordance with the mill's practice on hot-rolled billet material, are contained in Table 2.

TABLE 1.—*Chemical Composition of Material*

Heat	Composition, Per Cent									Residual Oxides
	C	Mn	P	S	Si	Ni	Cr	$\text{Al}_2\text{O}_3$	$\text{SiO}_2$	
A	1.06	0.23	0.015	0.021	0.21	0.10	0.05	0.005	0.004	0.025
B	1.07	0.24	0.010	0.014	0.23	0.09	0.03	0.007	0.007	0.021
C	1.04	0.18	0.008	0.013	0.24	0.10	0.03	0.006	0.005	0.021
D	1.04	0.21	0.007	0.014	0.22	0.09	0.04	0.008	0.004	0.038
E	1.06	0.27	0.013	0.016	0.25	0.09	0.04	0.006	0.005	0.028
F	1.06	0.23	0.010	0.015	0.22	0.09	0.06	0.008	0.005	0.034

#### INFLUENCE OF PRIOR STRUCTURE ON McQUAID-EHN TESTS

To determine the possible effect of various prior structural conditions upon the grain-size rating after the standard McQuaid-Ehn carburizing

treatment, representative disks (2 in. round by  $\frac{5}{8}$  in. thick) and bars (10 in. long by 1 in. in diameter) of the various heats were heat-treated so

TABLE 2.—*Characteristics of the Various Steels*

Heat	Penetration (Case Depth), $\frac{1}{64}$ In. <sup>a</sup>				Fracture Grain Size, No. (Shepherd Standard Values)				Hardenability, Core Depth, In.		McQuaid-Ehn Test, Grain Size
	Quenching Temperatures, Deg. F.								Oil-treated 0.300-in. Disk	Oil-treated and Annealed 0.343-in. Disk	
	1450	1500	1550	1600	1450	1500	1550	1600			
A	6½	7	8	11	9¼	8¾	8¼	7½	0.109–0.115	0.093–0.093	⅞
B	6½	7	8	9½	9¼	9	8¾	7½	0.094–0.094	0.085–0.085	⅞
C	6	6½	7½	8½	9¼	9¼	8¾	8¼	0.109–0.109	0.125–0.125	⅞
D	5½	6	7	9	9½	9¼	9	8¾	0.140–0.140	0.140–0.140	¾
E	7	8	8½	9	9¼	9	9	8	0.040–0.040	No core	¾
F	8	9½	13	16	9½	9	8	7½	No core	No core	¾

<sup>a</sup> Size of specimen: 3-in. long by  $\frac{3}{4}$  in. in diameter.

as to range from a completely spheroidized condition to a martensitic structure. The heat-treatments, together with the average hardnesses of the specimens before and after carburizing are recorded in Table 3.

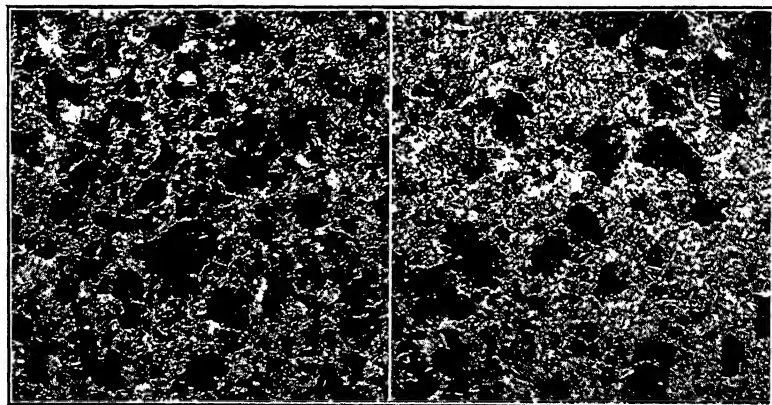


FIG. 7.

FIG. 8.

FIGS. 7-8.—EFFECT OF PRIOR STRUCTURE ON AUSTENITIC GRAIN SIZE.

Fig. 7. Brine-quenched and carburized.

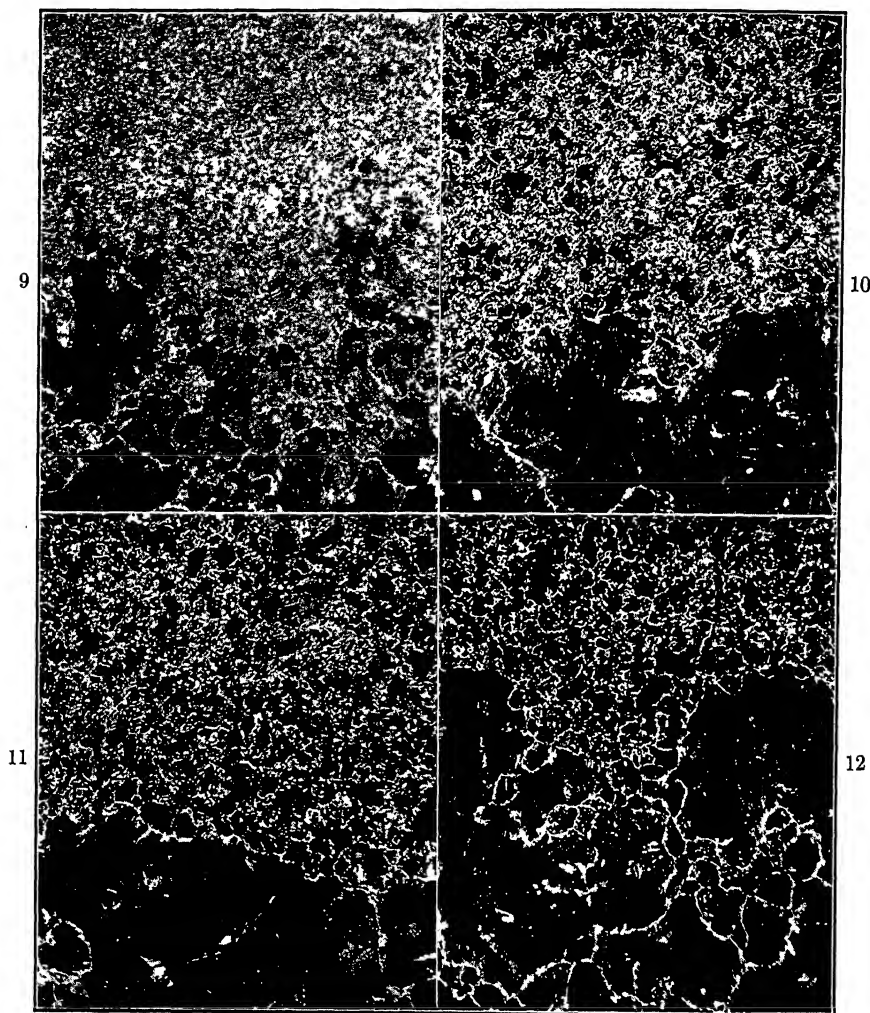
Fig. 8. Water-quenched and carburized.

Both etched in 1 per cent nital-picric acid solution.  $\times 100$ .

The grain-size conditions after carburization—that is, 8 hr. at 1700° F. (925° C.)—are illustrated in Figs. 7 to 12.

Table 3 shows that although the hardness values of the specimens before carburizing are different, they are practically constant after the McQuaid-Ehn treatment.

The marked influence of the structural condition, prior to carburization, upon the grain size of steel A is summarized in Fig. 13.



FIGS. 9-12.—EFFECT OF PRIOR STRUCTURE ON AUSTENITIC GRAIN SIZE.

Fig. 9. Oil-quenched and carburized.

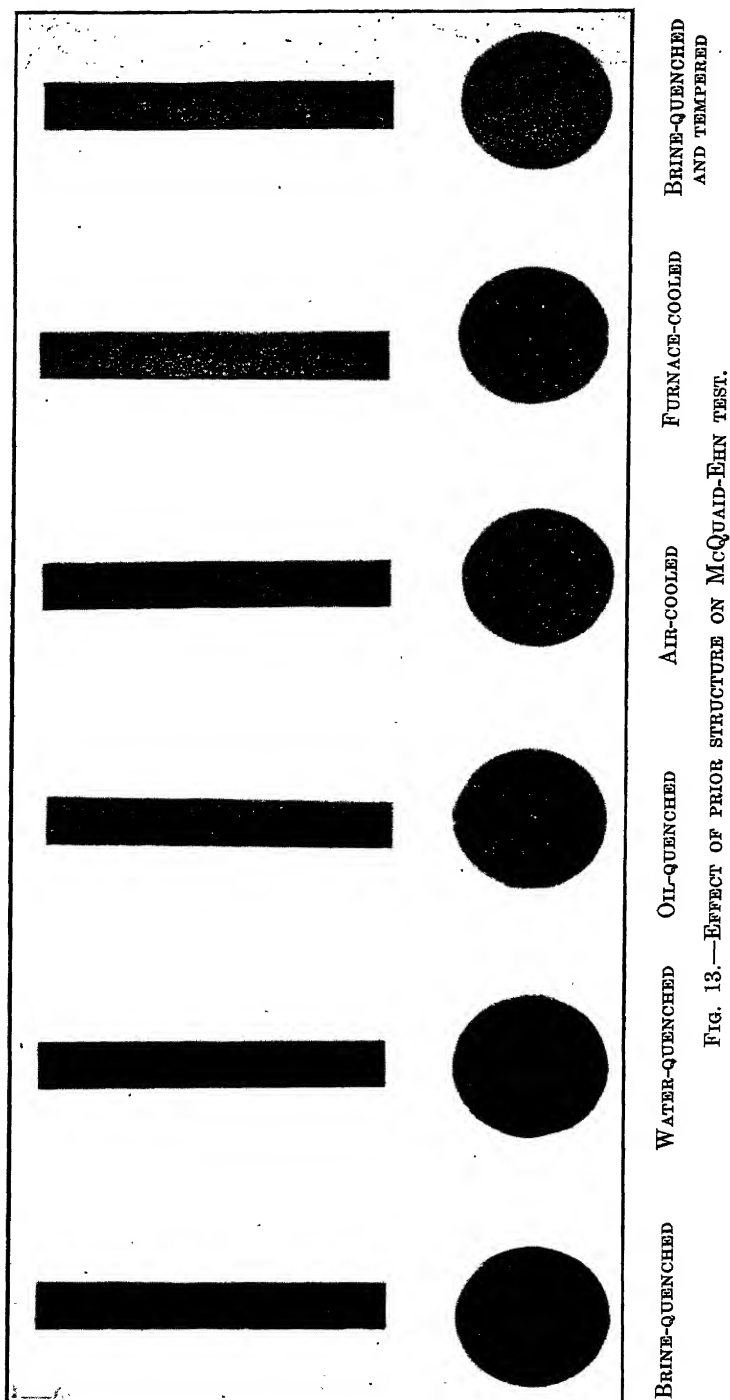
Fig. 10. Air-cooled and carburized.

Fig. 11. Furnace-cooled and carburized.

Fig. 12. Spheroidized (quenched and tempered) and carburized.

All etched in 1 per cent nital-picric acid solution.  $\times 100$ .

It will be noted that a change from a martensitic to a fully spheroidized prior structure effects a considerable enlargement of the austenitic grain size after the standard carburizing treatment, generally, although it was observed that the austenitic grain size gradually increased from the prior martensitic to the spheroidized condition.



The inherent characteristics of heats, which so markedly influence the general response of the material to heat-treatment, were also investi-

TABLE 3.—*Effect of Prior Structure and Carburizing on Hardness*

Heat-treatment at 1600° F.	Structure	Hardness, Rockwell C	
		Before Carburizing	After Carburizing
Brine quenched.....	Martensitic	6 $\frac{5}{8}$ 7	1 $\frac{7}{8}$ 8
Water quenched.....	Martensitic	6 $\frac{5}{8}$ 6	1 $\frac{7}{8}$ 8
Oil quenched.....	Troostitic	4 $\frac{6}{4}$ 7	1 $\frac{6}{4}$ 7
Air cooled.....	Sorbitic	3 $\frac{2}{3}$ 3	1 $\frac{6}{4}$ 6
Furnace cooled.....	Pearlitic	1 $\frac{3}{4}$ 9	1 $\frac{6}{4}$ 7
Quenched, tempered.....	Spheroidized	-2/-3	1 $\frac{6}{4}$ 7

gated as to their effect upon the austenite grain size after the standard carburizing treatment. While these inherent characteristics do have some bearing on this matter, all of the results obtained indicate that the

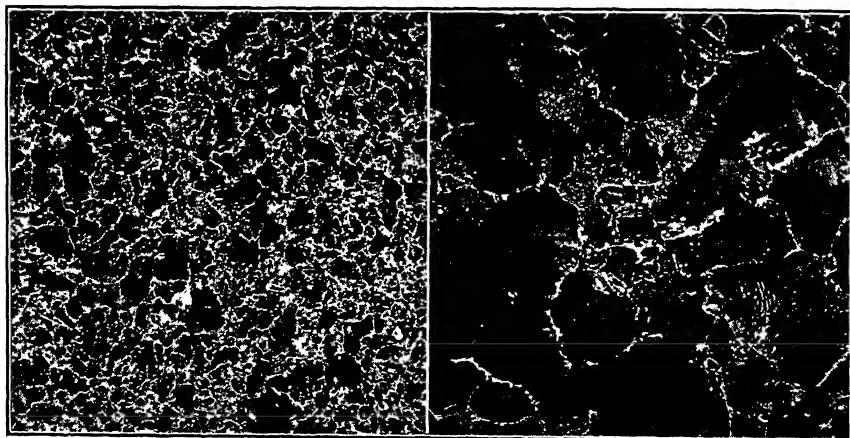


FIG. 14.

FIG. 15.

FIGS. 14-15.—EFFECT OF INHERENT CHARACTERISTICS ON AUSTENITIC GRAIN SIZE.

Fig. 14. Steel C carburized 8 hr. at 1700° F.

Fig. 15. Steel B carburized 8 hr. at 1700° F.

Both etched in 1 per cent nital-picric acid solution.  $\times 100$ .

influence of prior structural conditions tend to overshadow the possible effects of such inherent characteristics. Figs. 14 and 15 are indicative of this, because both steels shown, while different in their inherent characteristics, respond more in accordance with their prior structural condition than with their inherent characteristics. (The inherent characteristics of these two steels, as measured by the Shepherd<sup>2</sup> test

<sup>2</sup> B. F. Shepherd: The P/F Characteristics of Steel. *Trans. Amer. Soc. Metals* (1924) 22, 979.

of hardenability and penetration fracture grain size (P/F), are given in Table 4.)

# EFFECT OF HOT-WORKING AND COLD-WORKING UPON AUSTENITIC GRAIN SIZE

Since the structural condition prior to carburizing yielded such marked variations in the austenitic grain size as obtained by the McQuaid-Ehn test, an effort was made to determine the possible effects of hot and cold deformation. The former (hot-working) was accomplished by forging

TABLE 4.—*Penetration and Fracture Grain Size of Steels B and C*

Temperature, Deg. F.	Penetration <sup>a</sup>		Fracture Grain Size	
	Steel B	Steel C	Steel B	Steel C
1450	6½	6	9¼	9¼
1500	7	6½	9	9¼
1550	8	7½	8¼	8¾
1600	9½	8½	7½	8¼
1650	11	9	7½	8
1700	13½	9½	7½	7¾
1750	No core	10	Coarse	7½
1800	No core	12	Coarse	6¾
1900	No core	18	Coarse	5¾
2000	No core	No core	Coarse	Coarse

<sup>a</sup> Size of specimen, 3 in. long by ¾ in. in diameter.

material at elevated temperatures, noting: (1) the influence of forging temperature (constant reduction), (2) the effect of reduction (constant temperature).

*Effect of Hot Work.*—The influence of hot-working upon the austenitic grain size, as obtained after the McQuaid-Ehn treatment, is illustrated in Fig. 16, where A, B, and C demonstrate the effect of forging temperatures upon the condition of the austenitic grain size. The phenomena illustrated were found by upsetting bars (12 in. long by 3 in. dia.) at 1800° F. (980° C.), 2000° F. (1090° C.) and 2200° F. (1200° C.) to a constant size (3 in. long by 6-in. dia.). After cooling to room temperature, the bars were sectioned, surface ground, polished and carburized 8 hr. at 1700° F.

With increasing forging temperature, the depth of carburization and the grain size increased progressively.

The effect of variation in reduction at a constant hot-working temperature was recorded by heating bars (10 in. long by 2-in. dia.) to 2000° F. (1090° C.) and quickly forging them to a point. After cooling to room temperature, the bars were surface ground and car-

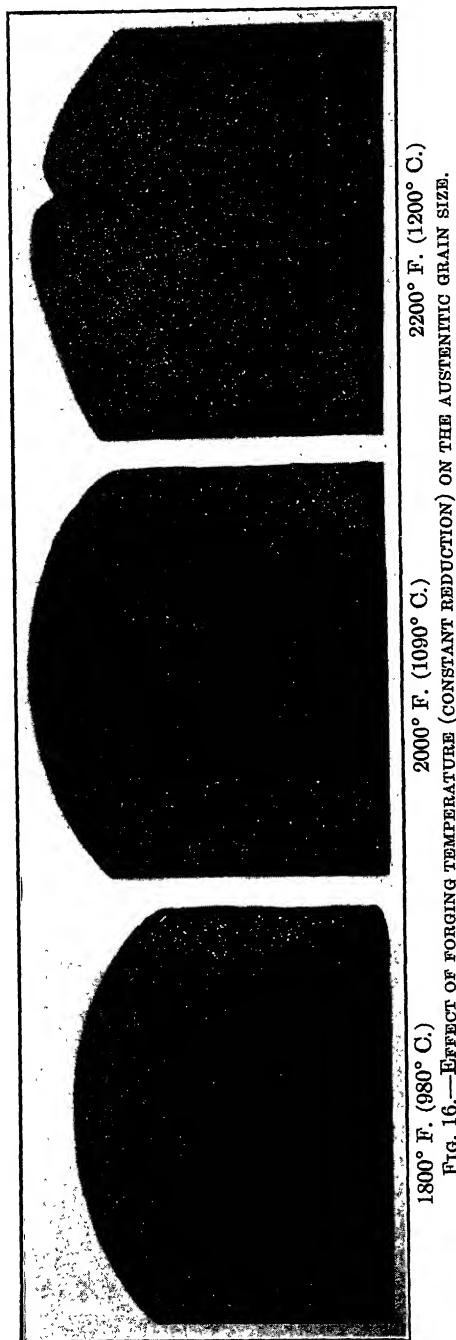


burized 4, 8 and 16 hr. respectively, then cut longitudinally through the center and polished.

Fig. 17, carburized 8 hr. at 1700° F. (925° C.), shows that at constant temperature the amount of reduction influences the austenitic grain size; i.e., the coarsening range. Figs. 18 and 19, taken at the unworked and maximum reduced sections, illustrate the change in grain size after the McQuaid-Ehn test, due to variations in the amount of reductions.

These results are in general agreement with the findings of Dr. Grossmann<sup>3</sup>, that in a medium carbon steel, containing less than 50 per cent of carbon, hot-working progressively lowers the coarsening temperature and increases the susceptibility to grain growth.

*Influence of Cold Work.*—The effect of cold work on the austenitic grain size was first determined by Brinelling (2-in. dia.) disks, using the standard 3000-kg. load, removing the impressions and carburizing 8 hr. at 1700° F. After carburization, the disks were ground, polished and etched in 5 per cent nital (Fig. 20). The areas where the Brinell marks occurred appear as fine-grained circles. Carburization of all cold-worked disks, regardless of heat, showed similar results, although in different degrees of intensity—the disks



<sup>3</sup> M. A. Grossman: Grain Size in Metals with Special Reference to Grain Growth in Austenite. *Trans. Amer. Soc. Metals* (1934) **22**, 10.

of some heats exhibited fine-grained zones in a coarse-grained matrix, while others showed coarse-grained circles in a fine background. Whenever the circle grain structure was fine, the grain had a tendency to

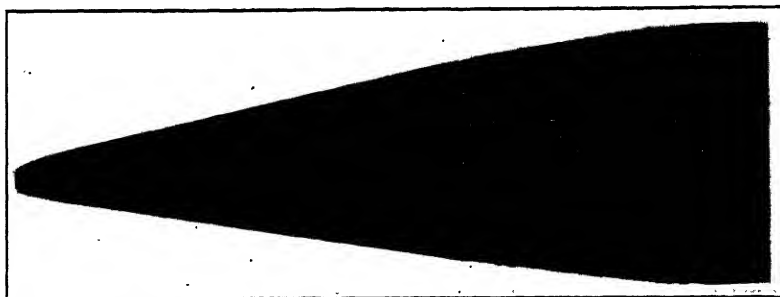
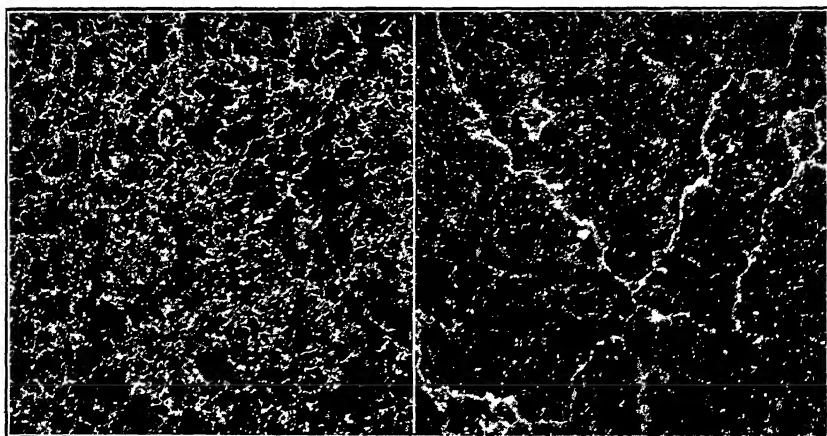


FIG. 17.—INFLUENCE OF HOT MECHANICAL DEFORMATION (CONSTANT TEMPERATURE) ON THE AUSTENITIC GRAIN SIZE.  
Forged at 2000° F. (1090° C.)

coarsen slightly a short distance from the periphery, indicating so-called critical grain growth, as observed by Professor Sauveur<sup>4</sup> in his cold-work experiments.

To obtain an intensification of cold work, annealed bars of 1-in. dia.



[FIG. 18.]

FIG. 19.

FIGS. 18-19.—INFLUENCE OF MECHANICAL DEFORMATION ON AUSTENITIC GRAIN SIZE.

Fig. 18. Austenitic grain size of unworked bar.

Fig. 19. Austenitic grain size of hot-worked bar.

Both etched in 1 per cent nital-picric acid solution.  $\times 100$ .

were bent in a tensile machine and carburized 8 hr. at 1700° F. After

<sup>4</sup> A. Sauveur: *Metallography and Heat Treatment of Iron and Steel*, Ed. 4. New York, 1936. McGraw-Hill Book Co.

carburizing, the bent bars were cut longitudinally through the center and polished. The results obtained are illustrated by one of the bars (Fig. 20), which shows excessive grain growth during carburization.

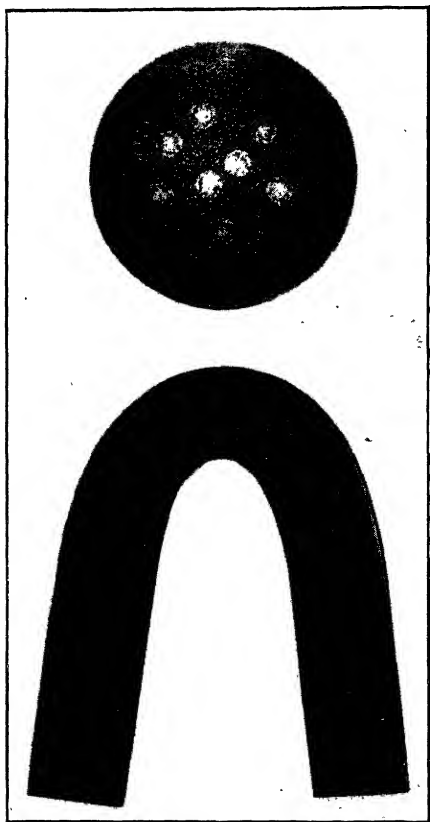


FIG. 20.—INFLUENCE OF COLD WORK ON AUSTENITIC GRAIN SIZE.

Fig. 20 also contains a photograph of a carburized disk showing the Brinell marks.

*Cold Drawing.*—The results of the influence of cold drawing on the coarsening temperature, published by McCarthy<sup>5</sup>, were substantiated during the course of this investigation. The conclusions obtained by carburizing cold-drawn wire (steel E), after various reductions, are presented in Table 5, and show that as the amount of reduction increases, the coarsening range and temperature automatically become lower.

*Duplexing.*—During the investigation of the effect of cold work upon the austenitic grain size as developed by the McQuaid-Ehn treatment, it was noted that the most severe amount of cold working yielded a uniform, fine grain size with rather coarse carbide boundaries: less severe distortion produced a maximum amount of duplexing, which progressively diminished with less deformation.

This indicates that duplexing is an inhibited grain-growth phenomenon, resulting from a "critical" amount of cold work. Similar "duplexing" results have more recently been obtained by localized temperature differences in "hot" deforming the material.

### SUMMARY

The data presented in this paper clearly show that a number of variants may influence the austenite grain-size rating of steel: primarily, it is the prior structural condition of the material, which in turn is definitely dependent upon the heat-treatment of the material, the amount

<sup>5</sup> B. L. McCarthy: Grain Size and Its Influence on the Manufacture of Steel Wire. *Iron Age* (Oct. 10 and 17, 1935).

TABLE 5.—*Effect of Cold Drawing upon Coarsening Temperature*

Diameter, In.	Area, In.	Reduction, Per Cent	Rockwell B Hardness	Coarsening Temperature, Deg. F.	Time, Hr.
0.361	0.1023		91.8	1700	4
0.330	0.0855	16.5	99.3	1650	4
0.296	0.0642	37.3	102.6	1600	8
0.268	0.0564	44.8	103.4	1600	4
0.239	0.0448	56.3	103.6	1500	16
0.210	0.0346	66.2	106.3		
0.181	0.0257	74.8	107.1		

of hot or cold mechanical deformation and the inherent characteristics of the melt, which determines the austenitic grain size after the standard McQuaid-Ehn carburizing treatment.

In view of these results, it is recommended that the actual service conditions to which the material is to be subjected must be fully considered before a definite austenite grain-size range, as determined by the McQuaid-Ehn test, is specified. An austenite grain-size rating, if used and interpreted intelligently and with the proper precautions, can be made into a valuable test method—both by the steelmaker and consumer—to ascertain, check and compare the uniformity of various steels at definite stages during the processing of the material. But it is obvious that any variations and differences in the austenite grain size, which may be observed in the partly processed or finished-processed stock, are not necessarily inherent characteristics of the melt.

#### ACKNOWLEDGMENT

The authors desire to express their appreciation to the officers and members of the Crucible Steel Company of America and its subsidiary plant, the Halcomb Steel Division, for the interest and assistance that have made these investigations possible. Particularly, they wish to express their appreciation and thanks to Mr. R. H. Dougherty, Assistant to the President of the Crucible Steel Company, for his constructive criticism and pertinent suggestions.

#### DISCUSSION

(*Francis B. Foley presiding*)

A. SAUVEUR,\* Cambridge, Mass. (written discussion).—A great deal has been written recently in regard to what have been termed the “inherent grain size” and “inherent characteristics” of steel. While one may wonder whether the importance of the subject has not been exaggerated by some, we should be indebted to the authors of this paper for calling our attention to the possible influence of the prior microstructure on the austenitic grain size as determined, for instance, by the well-known

\* Professor of Metallurgy, Harvard University.

McQuaid-Ehn method. The authors report that, starting with steel that has been made martensitic by suitable quenching, the resulting austenitic grain size as ascertained by the McQuaid-Ehn test is smaller than if the steel had previously been made pearlitic or had been spheroidized, from which it would follow that in order to obtain accurately comparable results by that test, care should be taken to impart the same microstructure to all samples, conveniently the pearlitic structure. We naturally seek an explanation for this apparent influence of the prior microstructure. It is generally helpful to go back to fundamentals. All carbon steels, regardless of the thermal or mechanical treatments to which they may have been subjected, are aggregates of two constituents only; namely, alpha iron, which may contain a little carbon in solid solution, and cementite, leaving out of consideration a small amount of austenite that may be present in quenched steel. If the physical properties differ so greatly, it is due solely to the size of the alpha (ferrite) grains and the particle size of the cementite. In the martensitic condition there is minimum grain size of the alpha iron and minimum size of the cementite particles, hence maximum hardness. This condition I believe to be due to instantaneous aging in the quenching bath when the solvent gamma iron capable of retaining over one per cent carbon in solid solution is converted into alpha iron practically unable to retain any carbon in solution. It is a case of excessive supersaturation of the alpha iron followed by the immediate precipitation of the cementite in submicroscopic dimensions. In the pearlitic condition, still more so in the spheroidized condition, there are maximum grain size of alpha iron and maximum size of the cementite particles, hence maximum softness.

Let us now consider steel that has been made martensitic and the same steel in the pearlitic condition, both subjected to the McQuaid-Ehn test. After holding those samples at 926° C. (1700° F.) for 8 hr., we might reasonably expect that they would behave in the same way, both samples being converted into 100 per cent austenite, and we wonder why the steel originally pearlitic should have a larger austenitic grain. Does not this possibly indicate a relation between the original size of the alpha grain and the size of the resulting austenitic grain? A large alpha-grain structure, such as is present in pearlitic steel or to a greater degree in spheroidized steel, would result in a larger austenitic grain as found by the authors, while the extremely small size of the alpha grains in martensitic steel would result in smaller austenitic grains. If we knew more about the mechanism by which one or several alpha grains are converted into one or more austenitic grains, we could speak with greater assurance. It does not appear to me unwarranted, however, to conceive the possibility that when a mass of small alpha grains is converted into austenite the resulting austenite grains will be smaller than those resulting from the transformation of a mass of large alpha grains. The boundaries between alpha grains, more numerous in the first instance, may play a part in the mechanism of the allotropic transformation.

I was greatly interested in the results obtained by the authors in subjecting to the McQuaid-Ehn test a steel bar that had been cold-formed by bending (Fig. 20). Clearly carbonizing had taken place critically, precisely at those portions of the bar where we would expect maximum grain growth on reheating *below* the thermal critical range. Since, however, this bar was heated for 8 hr. at 950° C., we may well ask how grain growth could possibly affect the carbonizing. I venture the following explanation, while not unmindful of its somewhat speculative character: By cold-bending the bar, some portions of it were placed in a proper condition for grain growth to occur at a suitable temperature below the critical range. Such temperature was necessarily attained, as the bar was heated from room temperature to the carbonizing temperature, and grain growth did take place, although for lack of time at the proper temperature, the growth must remain very slight. It was sufficient, however, to exert an action during the carbonizing operation. In those portions the austenite grains were larger because they resulted from the allotropic transformation of larger alpha grains.

Larger austenite grains in turn permit the introduction of carbon in casehardening more readily than small grains, hence the results reported by the authors.

It should be added that in a slightly hypereutectoid steel such as the authors used grain growth after cold-work deformation cannot be very marked. Indeed, it is probably too slight to be readily detected under the microscope. It may be sufficient, however, and apparently is sufficient, to cause a greater carbon absorption during the case-carburizing operation.

E. C. BAIN,\* New York, N. Y.—The authors deserve high commendation for collecting and presenting the many pertinent data relating to grain size in steel. Some of these data are unusual and therefore of particular interest. We wish to make only one general suggestion, and that relates to the occasional use of the word “inherent” as qualifying grain size. So far as we are aware a specimen of carbon or low-alloy steel has an austenitic grain size only when heated to a temperature establishing the austenitic solid solution. This grain size may be estimated in the structure subsequently set up during cooling. Now, the austenitic grain size, even of this specimen, depends upon the temperature of heating, the rate of heating, and sometimes upon the duration of the heating. Thus the conditions of heating must be accurately defined if the grain size is to be stated significantly.

Many factors influence the actual austenitic grain size established in the *final* heating of a steel article—the one grain size of paramount importance in relation to final properties. In a billet, for example, many of these factors have not yet come into play; hence the precise grain-growth “pattern” of a rolled bar of steel is not as yet fully “built in” at the billet stage. With an ingot, especially, the subsequent operations may often profoundly influence the austenitic grain size, which may later be established in a forged or machined part ready for the final cooling, especially if the heating temperature is in the range 1650° to 1750° F.

To be sure, certain strong controlling tendencies, either towards early coarsening in heating or towards a reluctance to coarsen even at high temperature, are established in the molten steel and it is proper therefore to refer in such a broad way to heats, for example, inherently possessing a reluctance to coarsen; i.e., in brief, an “inherently fine-grained type of steel.” To speak, however, of an “inherent grain size” appears to be essentially inaccurate and probably misleading. It would appear vastly more useful to decide which grain size is significant, and therefore to be mentioned, and to define its conditions of establishment, than to seek to refer to an improbable “inherent” grain size.

C. S. BARRETT,† Pittsburgh, Pa.—There are two possible methods that might be added to the authors’ list for determining austenite grain size, for the sake of completeness: (1) the X-ray diffraction pattern made at elevated temperatures, and (2) the electron microscope operating at temperature—a microscope in which electrons are refracted by magnetic or electric lenses much as light is refracted in the ordinary microscope.

E. E. THUM,‡ Cleveland, Ohio.—I should like to raise one word of caution. All these are surface conditions and it does not altogether follow that the condition existing at the surface also exists to any great depth. Most of the surface methods, of course, have that objection.

R. SCHEMPF.—Professor Sauveur has brought out the point that possibly the keeping of the material at some critical temperature for longer or shorter periods of time

\* Metallurgist, U.S. Steel Corporation.

† Physicist, Metals Research Laboratory, Carnegie Institute of Technology.

‡ Editor, *Metal Progress*.

may influence the final grain size, and this may be an answer to the critical range and critical grain growth we have noted as occurring on certain spots in the specimen under consideration.

As to the various other means mentioned for the determination of the austenitic grain size at varying temperatures, we believe that these methods are probably good for some of us who are fortunate enough to have the necessary laboratory equipment available. However, in general, I have to confess that I am not very familiar with these methods, which will probably never come within the reach of the average metallurgist.

In answer to Mr. Bain's remarks on controlling grain size and inherent characteristics, although the word "inherent" is being used a great deal and often in the wrong sense, steel nevertheless still has something inherent in it, whether we call it grain size or by any other name. In regard to the factors that influence the austenitic grain size in the final heating of any steel specimen, the results of this paper are in complete agreement with Mr. Bain's discussion, and illustrate that the subsequent operations may either accentuate or diminish the austenitic grain-size rating of the ingot or billet material.

F. B. FOLEY,\* Philadelphia, Pa.—The point is well taken that steels have inherent characteristics which, for a given set of conditions, influence results regardless of apparent identity of chemical composition.

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\* Superintendent of Research, The Midvale Co.

## Constitution of High-purity Iron-carbon Alloys

BY ROBERT F. MEHL\* AND CYRIL WELLS,† MEMBERS A.I.M.E.

(New York Meeting, February, 1937)

THE purpose of this investigation was to prepare high-purity iron-carbon alloys, to determine as precisely as possible the  $A_3$ (GOS), the  $A_{cm}$ (SE), and the  $A_1$ (PSK) transformation temperatures in the meta-stable iron-iron carbide system (up to 1.4 per cent C), and to study the influence of carefully controlled and constant rates of heating and cooling ( $\frac{1}{8}$  to 2° C. per minute) upon the transformation temperature and upon the resulting microstructure. Apart from the general metallurgical importance attending the completion of such a task, it will be noted that highly precise transformation temperatures are of interest and importance in the thermodynamic study of this system<sup>1</sup>.

Several determinations of the iron-iron carbide diagram have been made<sup>2</sup>. These suffer generally from the low purity of the alloys used, and from the application of methods of investigation of low sensitivity. Attempts to compare and weight the many data available in an effort to construct as accurate a diagram as possible have, in the main, been unsuccessful. In general, the wide differences in the results of different workers, the lack of complete analytical data, the omission of important details relating to the heat-treatment of the alloys, and the meager description of the methods of investigation applied, render such a process of averaging nearly meaningless. It may be seen from the summaries by Epstein<sup>2</sup> and Körber and Olsen<sup>1</sup> that variations as great as 30° C. exist in the reported data on the  $A_3$  temperatures in iron-carbon alloys. Fortunately, the  $A_3$  temperature in pure iron is now known to be 910° C.  $\pm$  1° C.<sup>3</sup> The best recent work on iron-carbon alloys is that of Esser<sup>4</sup> on hypoeutectoid steels and that of Sato<sup>5</sup> on both hypoeutectoid and hyper-eutectoid steels.

Esser made a dilatometric and magnetic study of iron and iron-carbon alloys containing 0.06 to 0.86 per cent C, for which a high purity is claimed. Presumably the electrolytic iron was reasonably pure, but the alloys contained considerable impurities, on the average totaling 0.35 per

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Manuscript received at the office of the Institute Dec. 1, 1936.

\* Director, Metals Research Laboratory, and Head, Department of Metallurgy, Carnegie Institute of Technology, Pittsburgh, Pennsylvania.

† Metals Laboratory, Carnegie Institute of Technology.

<sup>1</sup> References are at the end of the paper.



cent, including silicon, manganese, phosphorus, nickel, chromium and copper. Esser's dilatometric curves are excellent and show that the temperature gradient in the specimen during heating and cooling was unusually low, as evidenced by the fact that the  $Ac_3$  and  $Ar_3$  transformations in the iron and the  $Ac_1$  and  $Ar_1$  in the iron-carbon alloys used begin and end at the same temperature within  $1^\circ$  or  $2^\circ$  C. Unfortunately, however, Esser did not quote the rate of heating and cooling employed and evidently used only one rate, so that it is impossible to use his data in approximating the equilibrium temperatures.

According to Esser the eutectoid composition of iron-carbon alloys is at 0.86 per cent C, independent of the rate of heating and cooling. Upton<sup>6</sup> on the other hand believes that Esser's conclusions are incorrect; after studying Sato's data<sup>5</sup> Upton concludes that steels cooled at any practical rate have always a range of carbon composition within which the structure is completely pearlitic, and that this range of carbon composition increases as the rate of cooling is increased.

Sato, like Esser, used a fairly pure iron and prepared rather impure iron-carbon alloys. The total impurity in Sato's alloys increased with carbon content; the 1.55 per cent C alloy had 0.28 per cent of impurities of which 0.14 per cent was silicon. Analyses were made for only silicon, manganese, phosphorus, sulphur and copper. Like Esser, Sato used the dilatometric and magnetic methods of investigation. The dilatometric curves obtained are inferior to Esser's, for they show considerable evidence of the presence of a temperature gradient in the specimens during heating and cooling which must have led to errors of several degrees in approximating the equilibrium temperatures.\* Sato, however, determined the critical equilibrium temperature by extrapolation from temperature points obtained at several different rates of heating and of cooling, thus also furnishing data on the degree of superheating and of supercooling at the different rates used. Of the five rates used in the study of hypoeutectoid alloys only two— $5^\circ$  C. and  $0.5^\circ$  C. per minute—were constant. In other cases only average rates may be read from the heating and cooling curves; the  $10^\circ$  C. per minute rate was fairly constant, but the others varied considerably. The rates used in the study of hyper-eutectoid alloys were more specific:  $20^\circ$ ,  $10^\circ$  and  $2^\circ$  for both heating and cooling. We shall see later that all these rates are too rapid for accurate work, for the degrees of superheating and undercooling are so great that extreme extrapolation is needed to approximate the equilibrium temperatures—the temperatures for zero rate.

Sato found the  $Ac_1$  temperatures to be practically the same in hypoeutectoid alloys at the respective rates of heating, whatever the carbon

---

\* A discussion of the probable error caused by temperature gradients in Sato's high-purity iron specimens has been given previously. It is probable that the errors are of about the same magnitude in his iron-carbon alloy data ( $5^\circ$  C. or so).

content: 728° C. at 0.5° C. per minute, 735° C. at 5° C. per minute, and 750° C. at 90° C. per minute. On cooling, however, the  $Ar_1$  temperature was found to be lower at lower carbon contents at a given rate of cooling. Since Esser's data agree well with Sato's taken at 5° C. per minute, we may assume Esser's rate must have had approximately this value.

Sato published several constitution diagrams representing the transformation temperatures at different rates of heating and cooling. These seem to show that the eutectoid composition is but little affected by the rate of heating, but considerably affected by the rate of cooling.

Sato used a linear rate-temperature scale, plotting the rates of heating to one side of a zero rate line and the rates of cooling to the other, and obtained the equilibrium temperatures by graphically determining the temperature at zero rate. Yap<sup>7</sup> proposed using a log rate-log temperature plot, while Upton<sup>6</sup> contended that better extrapolation could be obtained by plotting the cube root of the rate against temperature. These different graphical methods gave results differing by an average of 10°. There is no good reason to select one of these methods in preference to another, though Sato's method is least desirable, and accordingly the extrapolated results remain of uncertain validity.

The results of Sato's magnetic studies, like those of Esser, show the magnetic change on heating to be complete at about 775°, and the change to be wholly reversible, without hysteresis. He noted that  $A_0$  magnetic change in  $Fe_3C$ , in alloys with as little as 0.12 per cent C, to occur at about 200°. Sato found no evidence for a magnetic change in eutectoid and hypereutectoid alloys, at temperatures above the eutectoid, though it is believed by some Japanese workers that the Curie point extends into the austenite field and constitution diagrams have even been published showing this.

#### PREPARATION AND ANALYSIS OF HIGH-PURITY IRON-CARBON ALLOYS

Of the methods available for the preparation of high-purity iron-carbon alloys from the high-purity iron previously prepared<sup>3</sup>, that of gas carburization was chosen chiefly because it was found possible to prepare alloys of any desired carbon composition by a suitable selection of carburizing gas and carburization temperature which showed a high degree of homogeneity in the as-carburized condition. Furthermore, this method introduces the very minimum of impurities; all melting practices suffer from manifold opportunities of contamination from crucible, flux, and atmosphere.\* Pieces of hydrogen-purified carbonyl iron,

\* In connection with the preparation of pure alloys by carburization, the work on the equilibria between hydrogen-methane mixtures and gamma iron as summarized by Schenck<sup>8</sup> was of great value. This work indicates that high hydrogen-hydrocarbon gas ratios are necessary if carburization is simultaneously to be accompanied by rapid homogenization. Schenck states that an austenite containing 0.4 per cent C is in

2 by  $1\frac{1}{2}$  by  $\frac{1}{8}$  in., prepared as described previously<sup>3</sup> (analyses given in Table 1) was carburized in dipentene-hydrogen or dipentene-benzene (sulphur-free)-hydrogen mixtures at various temperatures between 850° C. and 1100° C. for various time periods between 24 and 100 hr., depending upon the carbon content of the alloy desired. The apparatus used for the carburization is shown in Fig. 1. An Armco iron tube *Q*, which had previously been thoroughly purified by long treatment in hydrogen at elevated temperatures (hydrogen was passed through the tube for 250 hr. at 1100° C.) served as the carburizing chamber. This tube was surrounded by a heat-resisting tube *N* (20 per cent Ni, 20 per cent Cr, 1 per cent Si, balance Fe) supported in a Globar furnace. These two tubes were brazed together at one end and through a thin-walled iron expansion

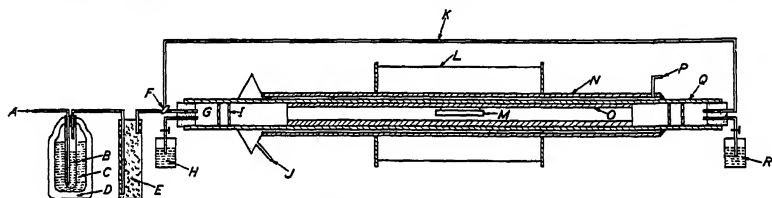


FIG. 1.—CARBURIZING APPARATUS.

- |   |  |
|---|--|
| A. Hydrogen inlet.                                      | J. Hydrogen inlet.   |
| B. Hydrocarbon.   | K. Glass tube conveying hydrogen to enter furnace tube from right. |
| C. Water at controlled temperature ( $\pm 3^\circ$ C.). | L. Globar furnace.   |
| D. Dewar flask.   | M. Specimen.   |
| E. Absorbent cotton.                                    | N. Heat-resisting tube.  |
| F. Three-way stopcock for reversing gas flow.           | O. Chemically pure magnesia tube.                                  |
| G. Inlet or outlet of gas to or from furnace.           | P. Hydrogen outlet.  |
| H. Gas outlet (when gas flow is right to left).         | Q. Armco iron tube.  |
| I. Radiation screen.                                    | R. Gas outlet, when gas flow is left to right.                     |

diaphragm at the other. The rubber tubing and the rubber stoppers used were sulphur-free. The iron sample *M* was suspended by fine high-purity iron wires from a chemically pure magnesia tube *O*. The purity of this tube is highly important: traces of silica in the presence of hydrogen are readily reduced and silicon transferred to the sample; no trace of silicon pickup in the sample could be observed in these experiments. The ends of the tube *Q* were protected from excessive heating by radiation screens *I*. Hydrogen was passed between tubes *Q* and *N* during the carburizing treatment, to prevent contamination and to prolong the life of the tubes. Hydrogen was passed through the liquid hydrocarbon *B* at a rate of 1 cu. ft. per hour; the liquid hydrocarbon was maintained at an approximately constant temperature ( $\pm 3^\circ$  over a 12-hr. period) by a water jacket *C* in a Dewar flask *D*. The hydrogen-hydrocarbon mixture was first passed

equilibrium at 1025° with methane at a partial pressure of 3.5 mm. The hydrocarbons used were selected to give a vapor pressure in this neighborhood in the temperature range 0° to 35° in the hydrocarbon saturator. Dipentene and mixtures of dipentene-benzene were finally selected as most useful.

through absorbent cotton *E*, then over the sample *M*, and finally out of the apparatus through water *R*. The direction of gas flow was reversed every 12 hr. To increase the hydrocarbon-hydrogen ratio, and thus to increase the carbon content of the alloy, the temperature of the liquid hydrocarbon saturator was raised, and vice versa. Liquid hydrocarbon temperatures as low as 0° C. and as high as 35° C. were employed in preparing the higher carbon alloys. For preparing alloys with 0.1 to 0.4 per cent C, dipentene was the only hydrocarbon used, with the carburization time varying between 24 and 50 hr. For higher carbon alloys dipentene-benzene mixtures (1 to 3 c.c. of benzene per 30 c.c. of dipentene) were employed, and the average time period increased to 75 hr.\* In preparing alloys with 0.90 to 1.4 per cent C, a lower carburizing temperature was chosen, and the percentage of benzene in the liquid hydrocarbon increased; in order to rectify losses, 3 c.c. of benzene was added to the dipentene every 12 hr. For alloys from 0.9 to 1.0 per cent C the carburizing temperature was 850°; for alloys from 1.0 to 1.1 per cent C the carburizing temperature was 900°; for alloys from 1.2 to 1.4 per cent the carburizing temperature was 1000°; the temperature of the liquid hydrocarbon was maintained at 35° throughout.

TABLE 1.—*Chemical Analyses of Iron Used for Carburization<sup>a</sup>*

Impurity	Number of Iron		Impurity	Number of Iron	
	1	3		1	3
Cu	0.0033	0.0012	Mo	0.002	0.005
Ni	0.0054	0.0068	C	0.0012	0.0018
S	0.00013	0.00005	P		<0.005
Si	0.002	0.002	O <sub>2</sub>		0.002
Sn		<0.001	N <sub>2</sub>		0.003
Mn	<0.004	<0.004	H <sub>2</sub>		0.0005
Cr	<0.0005	<0.0005			

<sup>a</sup> Spectroscopic analyses showed presence of traces of Cu, Ni, Si, Sn, Mn, Cr and Mo.

Thus, the hypoeutectoid alloys were prepared by carburizing in proper gas mixtures until the concentration of carbon in the alloy in equilibrium with the gas mixture was reached; for this reason the alloys were homogeneous as carburized. The hypereutectoid alloys, on the other hand, were carburized in gas mixtures the compositions of which were not carefully controlled but which possessed the minimum percentage of hydrocarbon to saturate the iron along the  $A_{cm}$  line at the carburization temperatures chosen; these alloys, therefore, should be and were homoge-

\* After several carburizing experiments much carbon was found deposited in tube *Q*; in the vicinity of the hottest part, the tube itself was naturally found to be highly carburized. With such a tube it was unnecessary to add benzene to the hydrocarbon in preparing alloys with carbon as high as 0.80 per cent.

neous as carburized. The homogeneity of the full range of alloys may be judged from the typical microstructures shown in Figs. 2 to 5; it will be shown later that the dilatometric results gave additional evidence of homogeneity. When, as in a few instances, the alloys were not homogeneous as carburized, owing to failure in control, homogenizing treatments were employed (Fig. 6).\*

The analyses of the alloys prepared and used are given in Table 2. Some 60 alloys in all were made, but only those that had been analyzed and used in determining critical temperatures are reported in Table 2.

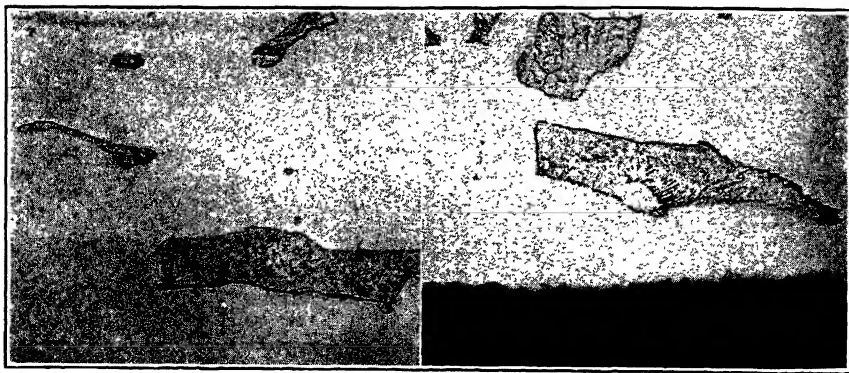


FIG. 2.

FIG. 3.

FIG. 2.—ALLOY 0.20 PER CENT C. SHOWING UNIFORM DISTRIBUTION OF CARBON DURING CARBURIZATION AND ALSO LARGE CARBIDE MASSES FORMED ON COOLING.

Carburized in a hydrogen-dipentene mixture for 46 hr. at 1100° C. Cooled in carburizing furnace at 1° C. per minute. Etched with sodium picrate.

FIG. 3.—ALLOY 0.20 PER CENT C. SHOWING UNIFORM DISTRIBUTION OF CARBON AT EDGE OF SPECIMEN DURING CARBURIZATION.

Original magnification 250; reduced  $\frac{3}{4}$  in reproduction.

The specimens marked *D* in the table were taken after use in procuring dilatometric curves for the purpose of ascertaining any contamination that might have occurred. Copper, nickel and silicon were determined, for copper and nickel might be picked up from Monel metal parts adjacent to the specimen in the dilatometer, and silicon might have been transferred to the sample from silica parts. Lathe turnings from specimens F19, F20 and F21 (not shown in this table) were mixed and analysis performed on the mixture. The amount of copper pickup could be detected both chemically and spectroscopically, but amounted to only 0.003 per cent. No pickup of nickel or silicon could be detected. With the exception of samples F19 and F20, used for the analysis of nickel,

\* A chemical control on homogeneity was applied using Eggertz' colorimetric method for carbon. Filings taken from a 0.01-in. surface layer, and filings from the interior of the specimen invariably gave the same carbon content, within the limits of accuracy of the method, which is  $\pm 0.03$  per cent C.

silicon and copper, the carbon analyses on alloys with less than 0.80 per cent C were performed on the specimen after the dilatometric studies; for the two exceptions, carbon analyses were performed on sections of the carburized specimen adjacent to the piece used for dilatometry.

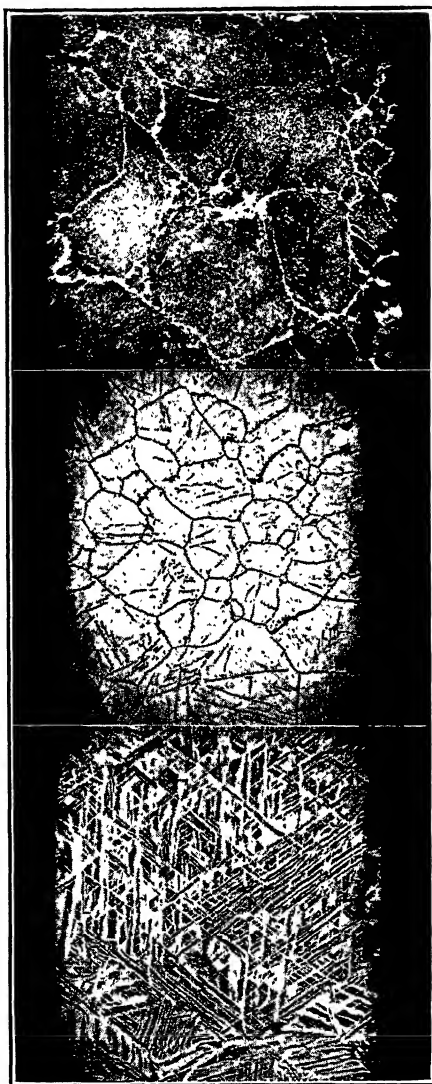


FIG. 4.

FIG. 5.

FIG. 6.

FIG. 4.—ALLOY 0.35 PER CENT C. GIVES EVIDENCE OF UNIFORM DISTRIBUTION OF CARBON IN AUSTENITE DURING CARBURIZATION.

Carburized in hydrogen-dipentene mixture for 50 hr. at 1100° C. Etched with nital.

FIG. 5.—ALLOY 1.25 PER CENT C. GIVES EVIDENCE OF UNIFORM DISTRIBUTION OF CARBON IN AUSTENITE DURING CARBURIZATION.

Carburized in hydrogen-dipentene benzene mixtures for 96 hr. at 1000° C. Etched with sodium picrate.

FIG. 6.—ALLOY 0.60 PER CENT C. SHOWING UNIFORM DISTRIBUTION OF CARBON AND NO DECARBURIZATION AFTER HOMOGENIZING.

Heated 175 hr. at 1100° C. in argon and cooled at 1° C. per minute. Homogenized after preparation.

Etched with nital.

!All × 20.

Standard chemical methods were used throughout. In the spectroscopic work, iron No. 3 (Table 1) was used as a comparison standard in order particularly to study contamination during carburization and during the dilatometric work. No detectable pickup of any element—except

TABLE 2.—*Chemical Analyses of Iron-carbon Alloys*

Alloy No.	Chemical Analyses, Per Cent					
	C			Cu	Ni	Si
			Average			
F3	0.134	0.136	0.135			
F41	0.164	0.156	0.160			
F20	0.280	0.280	0.280	0.006D	0.002D	0.002D
F4	0.302	0.302	0.302			
F19	0.310	0.310	0.310	0.006D	0.002D	0.002D
F12	0.340	0.342	0.341			
F40	0.456	0.460	0.458			
F44	0.486	0.488	0.487	0.004	0.002	0.005
F39	0.540	0.546	0.543		0.002	<0.0005
F29	0.580	0.578	0.579			0.002
F30	0.662	0.664	0.663	0.002		0.002
F31	0.662	0.668	0.665		0.002	<0.0005
F32	0.77		0.77			0.002
F56	0.84		0.84			
F57	0.95		0.95			
F8	0.96		0.96			
F54	1.00		1.00			
F58	1.01		1.01			
F38	1.17	1.17	1.170			
F36	1.25	1.25	1.250			
F32	1.37		1.37			

D indicates samples for analysis taken after specimens had been used in dilatometer; the duplicate C analyses for the two specimens F38 and F36 were taken from different parts of the single carburized pieces, thus demonstrating the uniformity of C distribution.

copper, as stated—could be detected spectroscopically\* in specimens that had been used in the dilatometer, or which had been heat-treated and quenched as noted below. Study was made of the spectral lines for nickel, silicon, tin, manganese, chromium, copper and molybdenum. The following alloys were studied spectroscopically: F14, F20, F21, F36, F38, F57; F19, F20, F21 and F57 were from dilatometric experiments and F36 and F38 were alloys used in the microscopic determination of the  $A_{cm}$  line.

Some hydrogen no doubt was present in the alloys as prepared, but since identical results were observed between comparable first and final tests in each series, it is concluded that the amount remaining after the vacuum treatment in the first test was insufficient to affect the results. Any hydrogen remaining after the first test would be further reduced by the vacuum treatments in subsequent tests.

\* A Hilger quartz spectrograph, type E, was used for the spectroscopic work.

## METHODS USED

The differential dilatometric method of investigation was used in the determination of the  $A_3$  and  $A_1$  temperatures and in the study of the influence of rate of heating and cooling on  $A_{cm}$  temperatures. Its use for the determination of the  $A_{cm}$  line proved to be very limited, and the method of studying structural changes by the microscope after prolonged heat-treatments proved to be much more satisfactory. Thermomagnetic and thermal methods were also used, but their utility is much inferior to the dilatometric method.

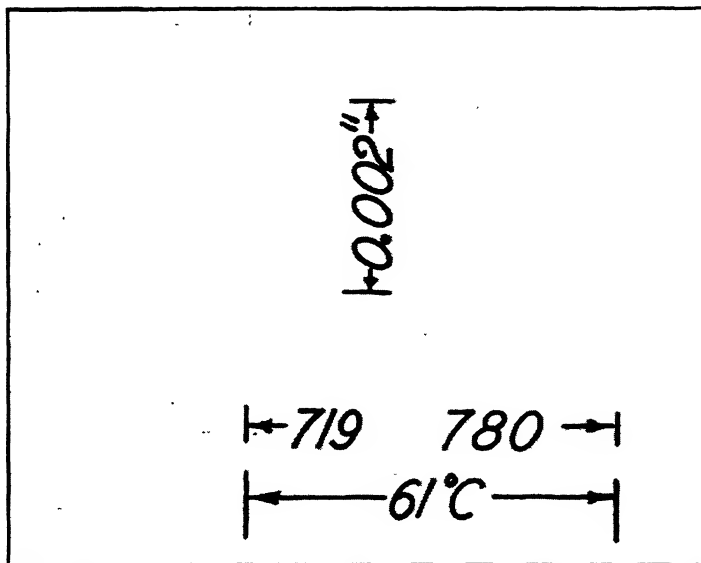


FIG. 7.—TYPICAL DIFFERENTIAL DILATOMETRIC-TEMPERATURE COOLING CURVE. ORIGINAL CURVE; NOT TRACED. ALLOY 0.457 PER CENT C. RATE OF COOLING  $2^{\circ}\text{C. PER MINUTE}$ .

*Dilatometric and Thermal Methods.*—A detailed description of the precision recording differential dilatometer used in this study has been given. The specimens, 1 by  $\frac{3}{8}$  by  $\frac{1}{8}$  in., were heated in a vacuum sufficiently high (about 1 micron) to prevent decarburization. The dilatometric data obtained are good to  $\pm 1^{\circ}\text{C}$ . To secure this precision, it is necessary to test the behavior of the instrument very carefully from time to time and to pay particular attention to thermometry.\* Temperature gradients within the specimen were measured from time to time during heating and cooling and these, if greater than  $0.5^{\circ}\text{C}$ . between the specimen ends, were reduced by a proper adjustment of separate heating

\* The precautions taken in making calibrations were identical with those described before.





*Magnetic Analyses.*—The apparatus used for the thermomagnetic studies consisted primarily of a suitable furnace, evacuating system, magnetizing coil, search coil, compensating coil, and ballistic galvanometer. The magnetizing coil was 18 in. long and  $3\frac{1}{2}$  in. in diameter and had 1869 turns of copper wire wound on a water-cooled brass tube. The search coil was wound around the specimen (1 by  $\frac{1}{8}$  by  $\frac{1}{8}$  in.) but insu-

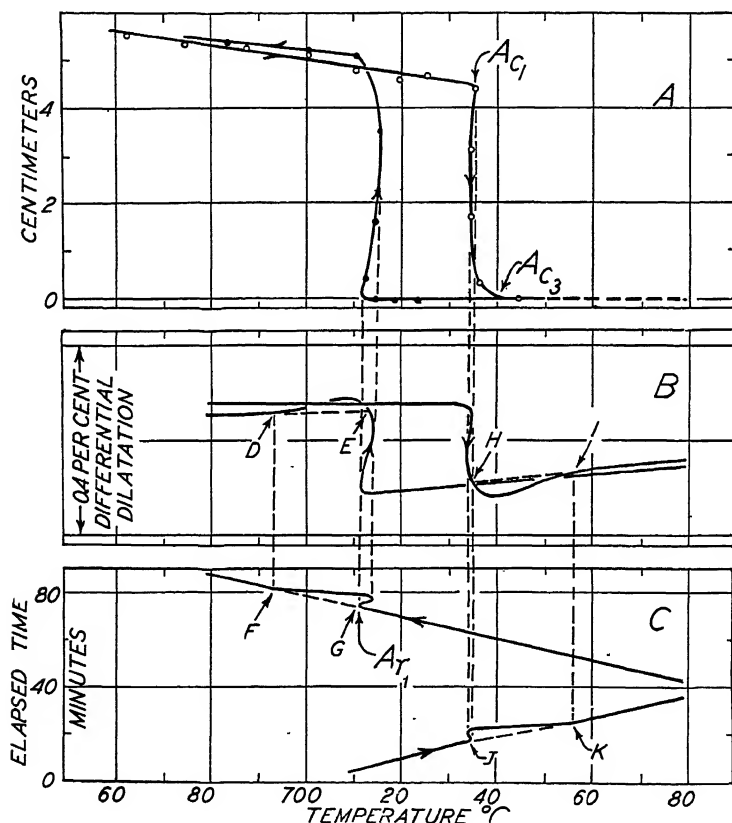


FIG. 9.—THERMOMAGNETIC, DIFFERENTIAL DILATOMETRIC AND THERMAL CURVES. CENTIMETERS (CURVES A) PROPORTIONAL TO MAGNETIC FLUX. ALLOY 0.77 PER CENT C. HEATING AND COOLING RATE,  $2^{\circ}$  C. PER MINUTE.

lated from it. The search coil and compensating coil were placed in close proximity in the furnace. By using the compensating coil no galvanometer throw occurred when the magnetizing field was reversed and when a nonmagnetic material was used. In most of the tests the magnetizing force was maintained constant at about 100 gilberts per centimeter (given by a current of 2 amp. through the magnetizing coil), though in some tests higher and lower values were used. Demagnetization of the specimen from the relative shortness of the specimen undoubtedly caused the effective field strength to be considerably below the impressed magnet-

izing force of 100 gilberts per centimeter, but since the primary point of interest was the temperature of magnetic change and not a determination of magnetic constants, this factor was not seriously considered. Specimens were heated and cooled at  $2^{\circ}$  C. per minute in all tests, except when the influence of the magnetizing force  $H$  on the degree of magnetic saturation of iron at a fixed temperature was studied. The deflections resulting from a reversal of magnetizing currents are measured on a circular scale and reported in centimeters. These are proportional to the magnetic flux in the specimen. Adjustments were made so that deflections of about 15 cm. were obtained for fully magnetic iron or iron-carbon specimens.

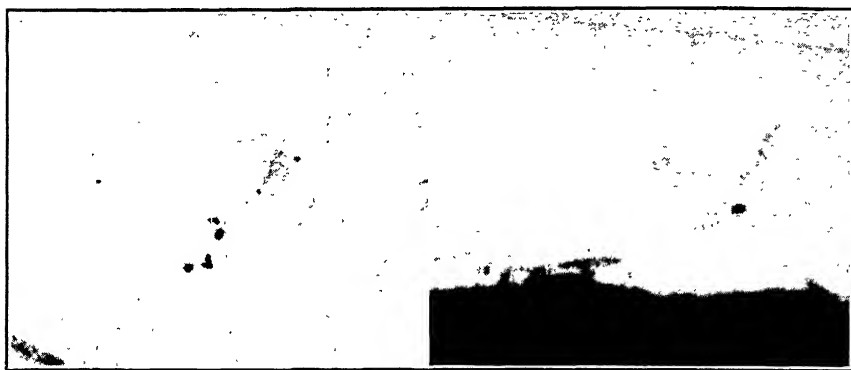


FIG. 10.

FIG. 11.

FIG. 10.—ALLOY 0.95 PER CENT C. SHOWS EVIDENCE OF CARBIDE, WHICH PERSISTED DURING HEAT-TREATMENT.

Heated to  $787^{\circ}$  C. for 20 hr. and quenched in oil. Center of piece. Etched with sodium picrate.

FIG. 11.—ALLOY 0.95 PER CENT C. THIS, WITH FIG. 10, SHOWS ABSENCE OF DECARBURIZATION AT SURFACE AND PRESENCE OF UNDISSOLVED CARBIDE NEAR SURFACE. Heated to  $787^{\circ}$  C. for 20 hr. and quenched in oil. Etched with sodium picrate.

Original magnification 2000; reduced  $\frac{1}{4}$  in reproduction.

*Comparison of Methods Used.*—A comparison of thermomagnetic, differential dilatometric and thermal curves is given in Fig. 9, curves A, B and C, respectively. In each case the steel was a 0.77 per cent C alloy, and the rate of heating and cooling  $2^{\circ}$  C. per minute. The  $Ac_1$  and  $Ar_1$  temperatures are apparently equally well determined by any one of these three methods. The thermal method as used in this investigation was not sufficiently sensitive to determine the  $Ac_3$  and  $Ar_3$  transformations at any of the rates used, and of little use in determining the  $Ac_1$  and  $Ar_1$  temperatures at the slowest rate,  $\frac{1}{8}^{\circ}$  C. per minute.

The differential dilatometric method proved to be excellent for determining the influence of rate of heating and cooling ( $\frac{1}{8}^{\circ}$ ,  $\frac{1}{2}^{\circ}$  and  $2^{\circ}$  C. per minute) on the  $Ac_3$  and  $Ar_3$  temperatures in alloys up to 0.70 per cent C, and on the temperatures of the  $Ac_1$  and  $Ar_1$  transformations throughout the whole carbon range. In this respect the dilatometric method has a wider application than the thermomagnetic method.

The anomalous length changes shown on the differential dilatometric curves immediately following the  $Ac_1$  transformation on heating and the  $Ar_1$  transformation on cooling require particular mention: these are caused by the temperature arrest in the specimen at the transformation. This arrest sets up a temperature difference between the specimen and the comparison pieces, which are composed of an iron-silicon alloy with 4 per cent Si and thus possess no transformation in the temperature range studied and thus also no arrest. This arrest is therefore equivalent to a contraction in the specimen on heating (Fig. 9, curves *B-HI*) and an



FIG. 12.

FIG. 13.

FIG. 12.—ALLOY 1.01 PER CENT C. SHOWING PROEUTECTOID CARBIDES AT GRAIN BOUNDARIES.

Heated at 1050° C. for 1¼ hr. and cooled at 10° C. per minute. Center of piece. Compare with Fig. 13. Etched with sodium picrate.

FIG. 13.—ALLOY 1.01 PER CENT C. SHOWS ABSENCE OF DECARBURIZATION AT SURFACE. MICROSTRUCTURE IDENTICAL WITH THAT IN FIG. 12.

Heated at 1050° C. for 1¼ hr. and cooled at 10° C. per minute. Etched with sodium picrate.

Original magnification 2000; reduced ¼ in reproduction.

expansion on cooling (Fig. 9, curves *B-DE*). This explanation is confirmed by the thermal curves, which show the anomaly to disappear when the thermal arrest is completed (as shown by a comparison of the dilatometric curves *B* with the thermal curve *C*, Fig. 9). This anomaly is thus an inevitable accompaniment of any differential method. The thermomagnetic method does not exhibit the anomaly; this method is suitable for determining the  $Ac_3$  temperatures just above the  $Ac_1$  temperature.

*Microscopic Determination of  $A_{cm}$ .*—The  $A_{cm}$  temperatures were determined by annealing experiments conducted at about 5° intervals, followed by quenching and microscopic observation of the presence or absence of undissolved  $Fe_3C$ . With good temperature control, this method proved highly sensitive, as may be seen in Figs. 10 and 11. The total volume of carbide undissolved in the 0.95 per cent C alloy at 787° C. after 20 hr. annealing is extremely small, showing that this temperature is very close to the  $A_{cm}$  temperature. In conducting this work, the specimens were

supported on chemically pure magnesia to avoid contamination and annealing was conducted in a high vacuum (about 1 micron) in order to

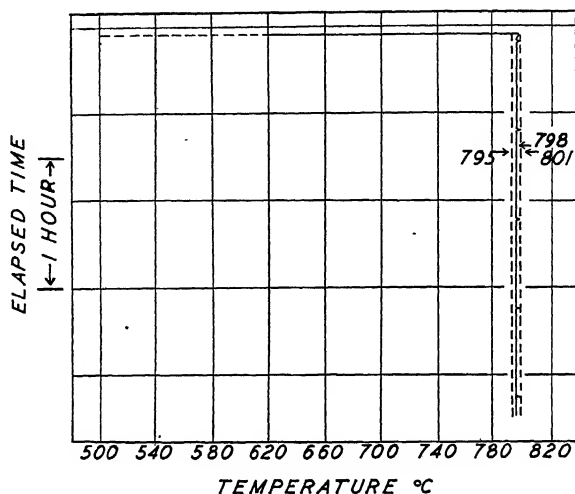


FIG. 14.—COPY OF TYPICAL TIME-TEMPERATURE RECORD DRAWN BY TEMPERATURE RECORDER.

Shows accuracy of temperature control and rapidity of quenching in tests used for the determination of the  $A_{cm}$  line.

avoid decarburization, a procedure which was successful, as may be seen in Figs. 12 and 13. The temperature was held constant to within  $\pm 1^\circ \text{C}$ .

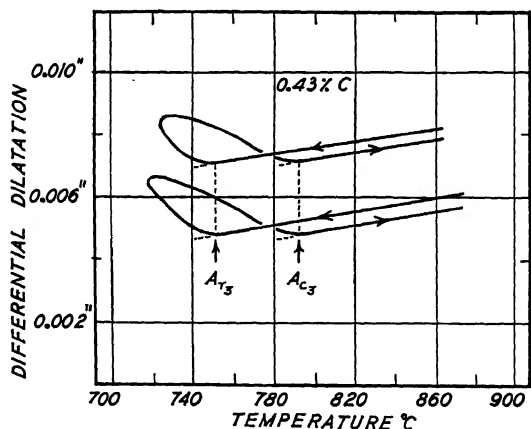


FIG. 15.—DIFFERENTIAL DILATOMETRIC-TEMPERATURE CURVES.

Showing reproducibility of results, and showing also absence of changes in composition (decarburization) during tests. Alloy 0.43 per cent C. Heating and cooling rates  $2^\circ \text{C}$ . per minute.

for several hours and then the specimen was rapidly quenched. Fig. 14 shows a temperature record of the quenching operation as given by the temperature recorder.

## RESULTS

*Factors Affecting Accuracy of Data*

Preliminary tests were performed to determine whether or not the vacuum used was adequate to prevent decarburization; no trace of decarburization could be discovered in the specimen even after heating to high temperatures and cooling several times. This is shown in Fig. 15 for an alloy with 0.43 per cent C, which had received a rather severe heat-treatment in the dilatometer; the upper curve shows the first dilatometric curve taken, and the lower curve that taken after the specimen had been heated to 870° and cooled several times and had been held at 870° for several hours. The upper and lower curves give a common value for the  $A_{c_3}$  temperature, namely 791° C., and for the  $A_{r_3}$  temperature, namely 751°. Decarburization would have altered these temperatures; a total change of 0.005 per cent C would have changed these temperatures by 1° C., and we may thus conclude that any loss of carbon must have been inferior to this. An alloy of approximately eutectoid composition, 0.77 per cent C, remained eutectoid throughout after having been annealed at 875° for 3½ hr. (Fig. 16).



FIG. 16.—ALLOY 0.77 PER CENT C. SHOWING ABSENCE OF DECARBURIZATION. Microstructure following dilatometric test after heating alloy at 875° C. for 3½ hr. and cooling at ½° C. per minute. Etched with nital. Original magnification 250; reduced ¼ in reproduction.

A study of graphitization in the alloys used has been made and will be the subject of a subsequent paper. The conditions that cause graphitization have been avoided in determination of the data given here.

The homogeneity of the as-carburized alloys may be seen from curves *C* and *D* in Fig. 22. These two curves were made on two samples cut from a single carburized piece; the curves show the  $A_{c_{\text{em}}}$  temperatures to be identical, namely 815°, within  $\pm 2^\circ$ . Since the  $A_{\text{em}}$  temperature is changed by 4° by a change in carbon content of 0.01 per cent, the two specimens must have had the same carbon content within  $\pm 0.005$  per cent. The homogeneity of the alloys is also shown by the fact that a relatively short preliminary heat-treatment (1 hr. at 860° for alloys between 0.2 and 1.0 per cent C) sufficed to render the alloys homogeneous enough to give the maximum attainable sensitivity on the dilatometric curves.

The curves given in Fig. 17 show that the break in the dilatometric curve at the  $A_{c_3}$  and  $A_{r_3}$  temperatures is much more sharply defined at

the slower rates of heating and cooling and that these transformation temperatures are therefore much more accurately determined at the slower rates. This is a fortunate circumstance, since the temperatures observed at the slowest rates are the closest to the equilibrium temperatures, and the extrapolation to the equilibrium temperatures at zero rate is thus the more accurate.

In a 0.31 per cent C alloy heated at  $2^{\circ}$  per minute, a difference of  $6^{\circ}$  is shown between the  $Ac_3$  temperature (vertical arrow, curve A, Fig. 17) and the point of intersection of the dotted lines; at the  $\frac{1}{2}^{\circ}$  rate this difference is  $3^{\circ}$  (curve B); at the  $\frac{1}{8}^{\circ}$  rate the difference is  $1^{\circ}$  or less (curve C). On cooling, an entirely analogous behavior is noted, curves F and G. After this alloy was cooled at the slowest rate,  $\frac{1}{8}^{\circ}$  per minute, a heating curve registered a much higher  $Ac_3$  temperature ( $828^{\circ}$ ). See

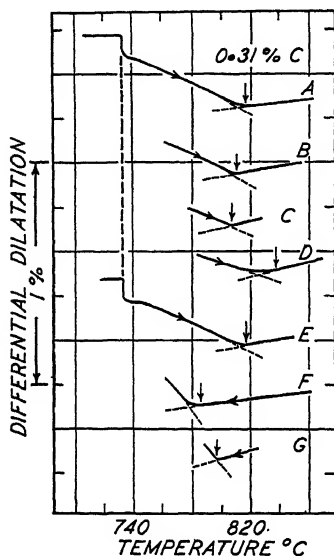


FIG. 17.

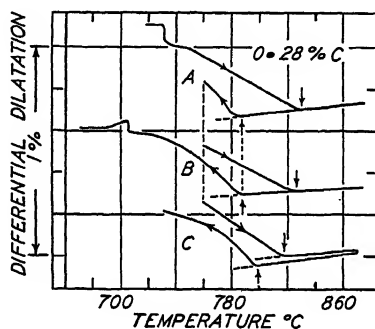


FIG. 18.

FIG. 17.—DIFFERENTIAL DILATOMETRIC-TEMPERATURE CURVES. ALLOY 0.31 PER CENT C.

Showing that accuracy in determination depends on rates of heating and cooling.

CURVE	RATE OF HEATING	CURVE	RATE OF HEATING
A	$2^{\circ}$ C. per minute	E	$2^{\circ}$ C. per minute
B	$\frac{1}{2}^{\circ}$ C. per minute		RATE OF COOLING
C	$\frac{1}{8}^{\circ}$ C. per minute	F	$2^{\circ}$ C. per minute
D	$2^{\circ}$ C. per minute	G	$\frac{1}{8}^{\circ}$ C. per minute

FIG. 18.—DIFFERENTIAL DILATOMETRIC-TEMPERATURE CURVES. ALLOY 0.28 PER CENT C.

Showing reproducibility of results after heating alloy at  $875^{\circ}$  C. for 1 hr.  $Ar_3$  temperature indicated by both cooling curves A and B is  $788^{\circ}$  C. ( $\pm 1^{\circ}$  C.).

Curves A: alloy heated to  $875^{\circ}$  C. at  $2^{\circ}$  C. per minute, held at temperature 1 hr., and cooled to  $760^{\circ}$  C. at  $2^{\circ}$  C. per minute.

Curves B: alloy reheated to  $875^{\circ}$  C. at  $2^{\circ}$  C. per minute, held 1 hr. at  $875^{\circ}$  C., and cooled to  $760^{\circ}$  C. at  $2^{\circ}$  C. per minute.

Curves C: alloy reheated to  $875^{\circ}$  C. at  $\frac{1}{2}^{\circ}$  C. per minute, held at  $875^{\circ}$  C. 1 hr., and cooled at  $\frac{1}{2}^{\circ}$  C. per minute.

curve D and compare with curve A), and a greater temperature range between this temperature and the temperature indicated by the intersection of the dotted curves. This effect originated in the relatively gross heterogeneity resulting from the preceding slow cooling. After holding at  $870^{\circ}$  for 1 hr. the alloy was restored to its original homogeneous

state, as shown by a comparison of curve *E* with curve *A*. The two  $Ac_2$  and the two  $Ac_1$  temperatures on curves *E* and *A* are identical within the experimental error,  $\pm 1^\circ$ .

The curves in Fig. 18 confirm the fact that annealing for 1 hr. at  $875^\circ$  C. is sufficient to render the alloy homogeneous and subsequently to give consistent and reproducible data to within  $\pm 2^\circ$ . After being carburized at  $1100^\circ$  C. and cooled in the carburizing furnace at the rate of  $1^\circ$  per minute, an alloy with 0.28 per cent C exhibited an austenitic grain size of one per square millimeter. This alloy was then heated in the dilatometer to  $875^\circ$  at the rate of  $2^\circ$  per minute and held there for 1 hr. (which was known from a separate experiment to give a grain size of 10 grains per sq. mm.), then cooled through the  $Ar_3$  temperature at the same rate to  $760^\circ$ , reheated at the same rate to  $875^\circ$ , cooled again at the same rate to  $760^\circ$ , reheated again to  $875^\circ$  at a rate of  $\frac{1}{2}^\circ$  per minute, and cooled to below the  $Ar_3$  temperature at a rate of  $\frac{1}{2}^\circ$  per minute; thus the alloy had passed through the  $A_3$  temperature six times (Fig. 18). Curves *A* and *B* show the thermal treatment to have been adequate to give identical  $Ar_3$  temperatures; the differences in the critical temperatures in curve *C* show merely the effect of rate. For alloys between 0.2 and 1.0 per cent C a heat-treatment consisting in an annealing at  $875^\circ$  for 1 hr. was therefore used between dilatometric experiments, for alloys of higher and of lower carbon contents higher annealing temperatures were used.

TABLE 3.—*Grain Sizes Developed in Iron-carbon Alloys<sup>a</sup>*

Alloy No.	Carbon, Per Cent	Treatment	Average Number Grains per Sq. Mm.
F1	0.05	1 hr. at $900^\circ$ C., quenched	1.5
F25	0.15	1 hr. at $875^\circ$ C., quenched	10 $\pm$ 3
F26	0.32	1 hr. at $875^\circ$ C., quenched	10 $\pm$ 3
F42	0.45	1 hr. at $875^\circ$ C., quenched	10 $\pm$ 3
F39	0.54	1 hr. at $875^\circ$ C., quenched	13 $\pm$ 3
F30	0.66	1 hr. at $875^\circ$ C., quenched	13 $\pm$ 3
F45	0.97	1 hr. at $1000^\circ$ C., quenched	13 $\pm$ 3
F36	1.25	1 hr. at $1000^\circ$ C., quenched	13 $\pm$ 3

<sup>a</sup> High-purity iron specimens heated at  $925^\circ$  C. for a few minutes, and high-purity iron-carbon specimens (0.05 to 0.56 per cent C) heated at  $1100^\circ$  C. for 1 hr. developed very large grains (1 grain or less per sq. mm.).

Table 3 lists the grain sizes developed in alloys of 0.2 to 0.7 per cent C on heating to  $875^\circ$  C. for 1 hr., of 0.05 per cent C on heating to  $900^\circ$  for 1 hr., and of the 0.97 to 1.25 per cent C on heating to  $1000^\circ$  for 1 hr. Differences in grain size, affecting the reactivity of the alloys, would affect the degree of undercooling and of superheating and thus affect the transformation temperatures. The grain sizes noted, however, were in a range where this effect was too small to be of importance.



### Dilatometric Results

Figs. 19 to 22 give typical differential dilatometric curves and show the influence of carbon content and of the rates of heating and cooling on the  $A_1$ ,  $A_s$  and  $A_{cm}$  transformation temperatures.

In low-carbon alloys, in the neighborhood of 0.15 per cent C, heated and cooled at a rate of  $2^\circ$  per minute, the contraction that takes place at constant temperature at  $Ac_1$  on heating is considerably greater than the expansion at  $Ar_1$  on cooling. The reason for this is not known.

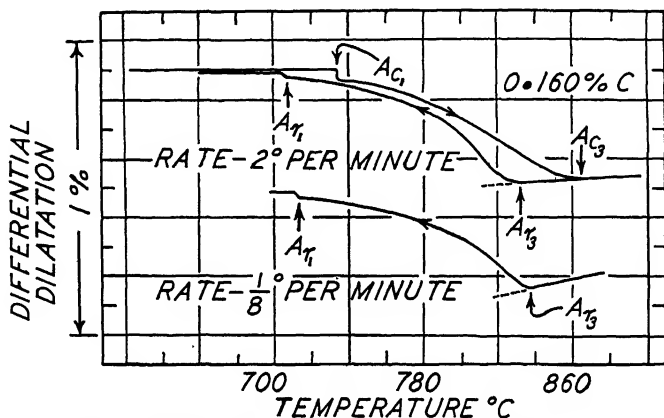


FIG. 19.—TYPICAL DIFFERENTIAL DILATOMETRIC-TEMPERATURE CURVES OF LOW-CARBON ALLOY.

Showing a greater contraction at  $Ac_1$ , than expansion at  $Ar_1$ .

It may be that the carbon concentration of the residual austenite on cooling below the  $A_1$  temperature is increased by a loss of ferrite induced by an inoculating effect of the great masses of proeutectoid ferrite; it is possible that the solubilities of carbon in  $\alpha$ -iron at the high  $Ac_1$  temperature and the low  $Ar_1$  temperature are quite different and that this affects the relative volumes of the various constituents, but this possibility is difficult to appraise. The temperature spread in the  $Ar_1$  transformation is believed to be due to the insufficiency in the heat generated to maintain the temperature constant; the effect is not noted in higher carbon alloys.

In a general way the cooling curves follow the course to be expected. At a  $2^\circ$  C. rate of cooling, as the temperature is decreased below the  $Ar_3$  temperature, the rate of  $\alpha$  nuclei formation in the considerably undercooled  $\gamma$  solid solution rapidly increases and then decreases. At a slower rate,  $1/8^\circ$  C. per minute, there is less undercooling below the  $A_s$  temperature and there is sufficient time for the generation of nuclei and the crystal growth to keep up with the temperature change; i.e., the transformation more nearly approaches equilibrium.

Apparently the temperatures of the  $Ac_3$  and  $Ar_3$  transformations are more affected by rate than those of the  $Ac_1$  and  $Ar_1$  transformations

(Fig. 20). By decreasing the rate from  $2^\circ$  to  $\frac{1}{8}^\circ$  C. per minute, the temperature difference between  $Ac_3$  and  $Ar_3$  is decreased from about  $50^\circ$  to  $18^\circ$  C., while that between  $Ac_1$  and  $Ar_1$  is only decreased from  $23^\circ$  to  $14^\circ$  C. The length of the specimen before and after test was not quite

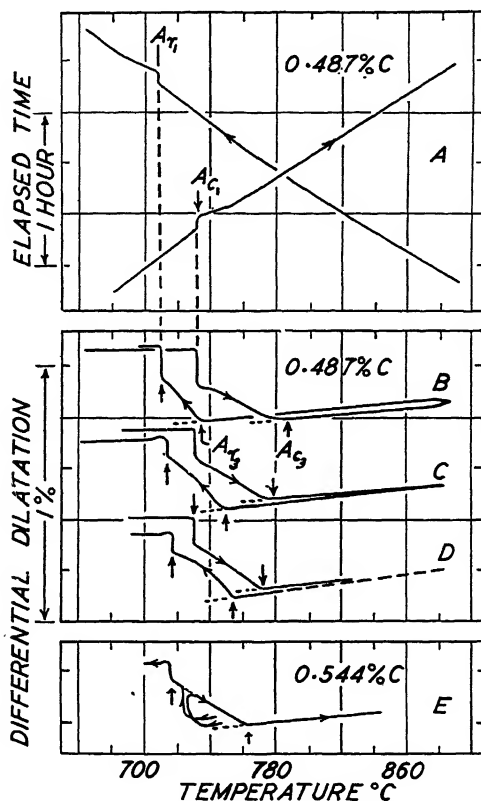


FIG. 20.—DILATOMETRIC CURVES.

Time-temperature cooling curves A, showing no evidence of the  $Ac_3$  or  $Ar_3$  transformations in an alloy with 0.487 per cent C.

Heating and cooling rate,  $2^\circ$  C. per minute.

Differential dilatometric-temperature curves B, showing good agreement with curves A with respect to  $Ac_1$  and  $Ar_1$  temperatures. Rate of heating and cooling:  $2^\circ$  C. per minute.

Curves C and D, heating and cooling rates:  $\frac{1}{2}^\circ$  C. per minute and  $\frac{1}{8}^\circ$  C. per minute respectively.

Curves B, C and D show influence of rate of heating and cooling on the  $A_3$  and  $A_1$  transformations.

Curves E, showing results of study of attainment of equilibrium (see text).

the same at temperatures below the transformations. These differences may be caused by experimental error, for the results were not reproducible in this respect—occasionally the length increased and occasionally decreased. In general, however, at the slower rates, and when the specimen had been heated for long periods at high temperatures, the specimens were shorter after the completion of the tests.

The thermal curves *A*, Fig. 20, are comparable with the differential dilatometric curves *B*. It is apparent that the  $Ac_3$  and  $Ar_3$  transformation temperatures may be readily determined by the dilatometric method, but not by the thermal method. The two methods gave results which agree to  $\pm 1^\circ \text{C}$ . for the  $Ac_1$  and the  $Ar_1$  temperatures.

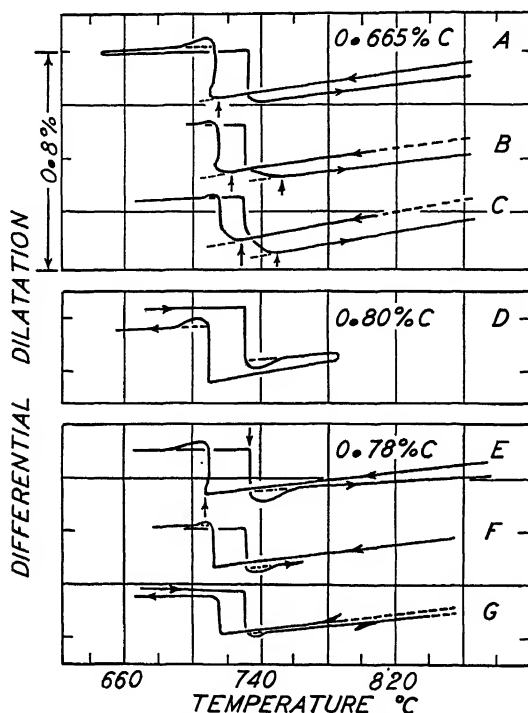


FIG. 21.—TYPICAL DIFFERENTIAL DILATOMETRIC-TEMPERATURE CURVES FOR HYPO-EUTECTOID ALLOYS OF COMPOSITION CLOSE TO EUTECTOID COMPOSITION. Showing the influence of rate on the  $A_3$  and  $A_1$  transformations.

HEATING AND COOLING		HEATING AND COOLING	
CURVES	RATE	CURVES	RATE
A	$2^\circ \text{C. per minute}$	E	$2^\circ \text{C. per minute}$
B	$\frac{1}{2}^\circ \text{C. per minute}$	F	$\frac{1}{2}^\circ \text{C. per minute}$
C	$\frac{1}{8}^\circ \text{C. per minute}$	G	$\frac{1}{8}^\circ \text{C. per minute}$
D	$2^\circ \text{C. per minute}$		

A comparison between the results shown by curves *D* and by curves *E* shows that the rate of formation of nuclei and of crystal growth is of great importance in determining the shape of the dilatometric curves. Curve *D* was taken at a rate of heating and cooling of  $\frac{1}{8}^\circ$  per minute. For curve *E*, the specimen was cooled from above  $A_3$  to  $730^\circ$  at the rate of  $2^\circ$  per minute and then to below the  $A_1$  temperature at the rate of  $\frac{1}{8}^\circ$  per minute, and in the other case the alloy was cooled from above  $A_3$  to  $735^\circ$  at  $2^\circ$  per minute and then heated at  $\frac{1}{8}^\circ \text{C. per minute}$  to above the  $Ac_3$  temperature. In the experiment shown in curve *E*, with much of the transformation displaced to a low temperature, more nuclei must

have been formed than in the experiment represented by curve *D*, and thus the part of the curve between  $A_1$  and  $A_3$  is much more nearly straight, for the greater number of nuclei must have assisted the alloy in approaching its equilibrium composition more rapidly. Thus the concave portion

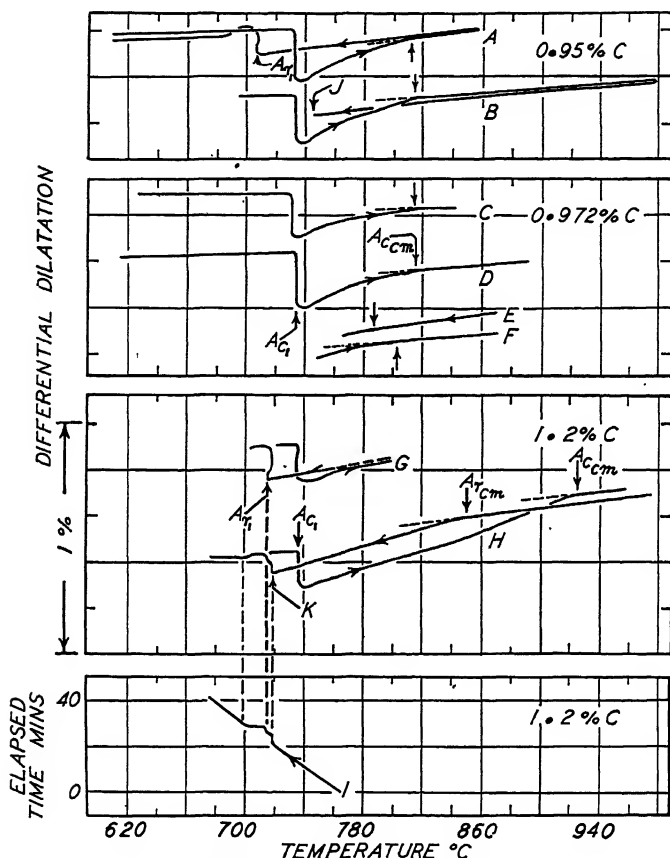


FIG. 22.—TYPICAL DIFFERENTIAL DILATOMETRIC-TEMPERATURE CURVES SHOWING DIFFICULTY IN DETERMINING  $A_{r_{cm}}$  TEMPERATURES DILATOMETRICALLY IN ALLOYS CONTAINING LESS THAN 1 PER CENT C (CURVES A, B AND E), AND RELATIVE EASE IN HIGH-CARBON ALLOYS (CURVE H).

Rate of heating and cooling, curves A, B, C, D, G, H and I, 2° C. per minute. Rate of heating, curve F,  $\frac{1}{8}$ ° C. per minute. Rate of cooling, curve E,  $\frac{1}{8}$ ° C. per minute.

of the cooling curve in *D* is probably caused by acceleration of transformation with increasing nuclei formation on cooling. In test *D* considerable ferrite was found segregated at the grain boundaries of the original austenite, resulting in a gross cellular microstructure. In test *E*, much less ferrite formed at the original austenite grain boundaries and the microstructure, exhibiting a Widmanstätten figure, was considerably more refined.

Curves showing the dilatometric behavior of the hypoeutectoid alloys close to eutectoid composition are given in Fig. 21. When the 0.665 per cent C steel is cooled at  $2^{\circ}\text{C. per minute}$ , its  $\text{Ar}_3$  temperature ( $716^{\circ}\text{C.}$ ) occurs so close to the  $\text{Ar}_1$  ( $711^{\circ}\text{C.}$ ) that the distinction between the  $\text{Ar}_3$  and the  $\text{Ar}_1$  temperatures on curve A may not be recognized. Figs. 25 and 26 show, however, the presence of proeutectoid ferrite and thus prove that the alloy experienced an  $\text{Ac}_3$  transformation; the two temperatures are apparently only  $5^{\circ}$  apart in this alloy. In alloys containing more carbon, no  $\text{Ar}_3$  transformation can be found at the rate of  $2^{\circ}$  per minute and dilatometric curves change direction sharply at the  $\text{Ar}_1$  temperature (curves D and E). The  $\text{Ac}_3$  transformation is not definitely indicated

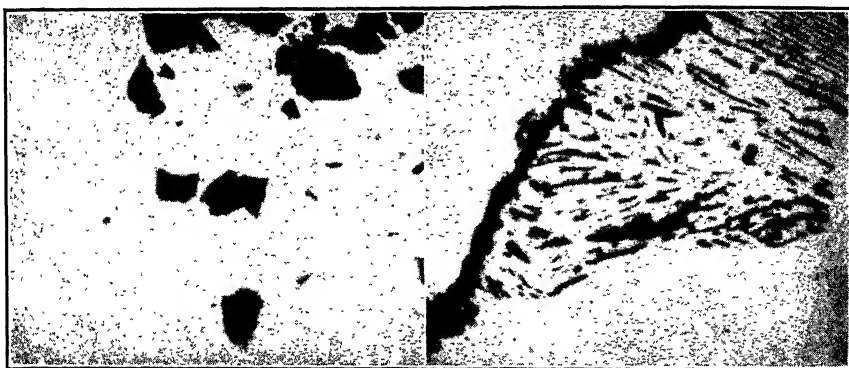


FIG. 23.

FIG. 24.

FIG. 23.—ALLOY 0.05 PER CENT C. SHOWS UNUSUAL DISTRIBUTION OF CARBIDE (BLACK) AND FERRITE (UNETCHED).

Alloy carburized in hydrogen-dipentene mixture at  $1200^{\circ}\text{C.}$  for 11 hr. and then cooled at  $1^{\circ}\text{C. per minute}$  in the carburizing furnace. Etched with sodium picrate.

FIG. 24.—ALLOY 0.20 PER CENT C. PEARLITE AND UNUSUALLY LARGE CARBIDE MASSES WERE FORMED DURING COOLING.

Alloy carburized in a hydrogen-dipentene mixture at  $1100^{\circ}\text{C.}$  for 46 hr. and cooled at  $1^{\circ}\text{C. per minute}$ . Etched with sodium picrate.

Original magnification 1500; reduced  $\frac{1}{4}$  in reproduction.

by the heating curve A, owing probably to the masking effect of the dilatometric anomaly associated with the latent heat. As the rate of heating and cooling were decreased, both the  $\text{Ac}_3$  and the  $\text{Ar}_3$  temperatures became more clearly defined (curves B and C).

The dilatometric anomaly at  $\text{Ac}_1$  and  $\text{Ar}_1$  transformations is most apparent in alloys of eutectoid composition when heated or cooled at the fastest rate ( $2^{\circ}\text{C. per minute}$ ). Curves D to G (Fig. 21) show the magnitude of this anomaly, and the effect of rate upon it.

Dilatometric curves for hypereutectoid alloys containing 0.95 per cent C, 0.972 per cent C and 1.2 per cent C are given in Fig. 22. Curves A show that the contraction during heating at the  $\text{Ac}_1$  transformation temperature is greater than the expansion during cooling at  $\text{Ar}_1$ . The explanation for this is probably the same as that given for the similar

phenomenon in hypoeutectoid alloys, except that in this case  $\text{Fe}_3\text{C}$  is the proeutectoid phase. Carbide precipitated from austenite causes a contraction, whereas the formation of ferrite causes an expansion. Thus in pearlite these two processes tend to neutralize each other. Fig. 27 shows that proeutectoid cementite formed on cooling the 0.95 per cent C alloy, though this is not shown by the dilatometric curves *A*. The alloy was heated at  $2^\circ \text{C. per minute}$  to  $980^\circ \text{C.}$ , then cooled at the same rate to a temperature of  $745^\circ \text{C.}$  and quenched (Curves *B*, Fig. 22). The microstructure showed evidence of carbides present at the quenching temperature.



FIG. 25.

FIG. 26.

FIG. 25.—ALLOY 0.665 PER CENT C. SHOWING CONSIDERABLE PROEUTECTOID FERRITE PRECIPITATED DURING COOLING.

Alloy heated at  $875^\circ \text{C.}$  for 1 hr. in dilatometric test (Fig. 21, curves *A*), and cooled at  $2^\circ \text{C. per minute}$ . Etched with nital. Original magnification 250; reduced  $\frac{1}{4}$  in reproduction.

FIG. 26.—ALLOY 0.665 PER CENT C. SHOWING LARGE MASSES OF PROEUTECTOID FERRITE WITH SUBSEQUENT FORMATION OF LARGE CARBIDE MASSES AND STILL LATER FORMATION OF LAMINATED PEARLITE AT  $\text{Ar}_1$ .

Alloy heated at  $875^\circ \text{C.}$  for 1 hr. and cooled at  $2^\circ \text{C. per minute}$ . Etched with nital. Original magnification 1500; reduced  $\frac{1}{4}$  in reproduction.

Attempts to make dilatometric analyses of hypereutectoid alloys containing below 1 per cent C were only partly successful, owing to the small change of slope in the dilatometric curves at the  $\text{Ac}_{\text{cm}}$  and the  $\text{Ar}_{\text{cm}}$  temperatures (see curves *E* and *F*). It is difficult to secure dilatometric data on these alloys using various rates of cooling, especially fast rates. Considerable carbide was precipitated above  $730^\circ \text{C.}$  in an alloy (0.972 per cent C) cooled at  $\frac{1}{8}^\circ \text{C. per minute}$  from  $840^\circ \text{C.}$  (Fig. 28) and yet the dilatometric cooling curve (curve *E*, Fig. 22) shows practically no evidence of a change of direction of the curve. A satisfactory dilatometric analysis of higher carbon alloys is much less difficult, as shown in curves *H* (Fig. 22), since the change of direction of the curves at  $\text{Ac}_{\text{cm}}$  and  $\text{Ar}_{\text{cm}}$  temperatures is much more pronounced.

The retention of a considerable amount of carbide in the 1.2 per cent C alloy during cooling at a rate of  $2^{\circ}$  C. per minute is probably responsible for the behavior of the alloy in the vicinity of the  $Ar_1$  temperature (Fig. 22, curves *H*, point *K*). It was observed that when the carbides were more completely separated on cooling before the  $Ar_1$  transformation temperature was reached, no irregularity at that temperature was observed (curves *G*). In order to separate the carbides more completely in test *G* than in test *H*, the alloy was cooled from  $980^{\circ}$  C. to  $760^{\circ}$  C. at

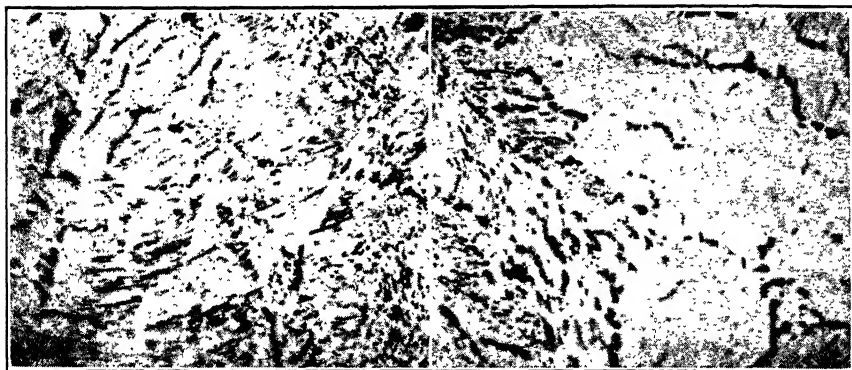


FIG. 27.

FIG. 28.

FIG. 27.—ALLOY 0.95 PER CENT C. SHOWING PROEUTECTOID CARBIDES (BLACK) PRECIPITATED ABOVE  $745^{\circ}$  C. THE DILATOMETRIC TESTS (DILATOMETRIC COOLING CURVES *A* AND *B*, FIG. 22) GAVE NO EVIDENCE OF THIS.

Cooled from  $980^{\circ}$  to  $745^{\circ}$  C. in a dilatometric test (curves *B*, Fig. 22), and then cooled at about  $50^{\circ}$  C. per minute. Etched with sodium picrate.

FIG. 28.—ALLOY 0.972 PER CENT C. SHOWS EVIDENCE OF CONSIDERABLE PROEUTECTOID CARBIDE FOUND ABOVE  $730^{\circ}$  C., THOUGH THE DILATOMETRIC TEST GAVE ONLY A VERY SLIGHT INDICATION OF THIS.

Cooled from  $875^{\circ}$  C. in dilatometric test (curve *E*, Fig. 22) at  $\frac{1}{8}^{\circ}$  C. per minute to  $730^{\circ}$  C. and then cooled at about  $50^{\circ}$  C. per minute. Etched with sodium picrate.

Original magnification 2000; reduced  $\frac{1}{4}$  in reproduction.

$\frac{1}{8}^{\circ}$  C. per minute, and then to below the  $Ar_1$  temperature at  $2^{\circ}$  C. per minute. The greater expansion at  $Ar_1$  shows that less carbide separated at  $Ar_1$ . It seems likely that considerable carbides were precipitated at the temperature indicated by *K* (curves *H*) and that simultaneously part of the  $A_1$  transformation occurred owing to the considerable disturbance created by the formation of carbide. It will be observed that point *K* (curves *H*) is below the  $A_1$  transformation temperature,  $723^{\circ}$  C. A comparison between the cooling curve *H* and the thermal curve *I* shows that the dilatometric and thermal results are in agreement with respect to this irregularity.

### *Thermomagnetic Results*

The shape of a thermomagnetic curve for iron and iron-carbon alloys depends on the magnitude of the magnetizing force used<sup>10,11</sup>. Above

certain minimum very high values of magnetizing force at which iron is completely saturated, the shape of the magnetic curve becomes independent of the magnetizing force.

The isothermal magnetic flux-magnetizing force curves of Fig. 29 (left)\* show the influence of the magnetizing coil current (proportional to  $H$ , the magnetizing force) on the degree of saturation of iron at various temperatures. As the temperature is increased, a lower magnetizing coil current is required to give magnetic saturation. This explains why in the vicinity of the Curie point ( $780^{\circ}\text{C.}$ ) the curves in Fig. 29 (right) have

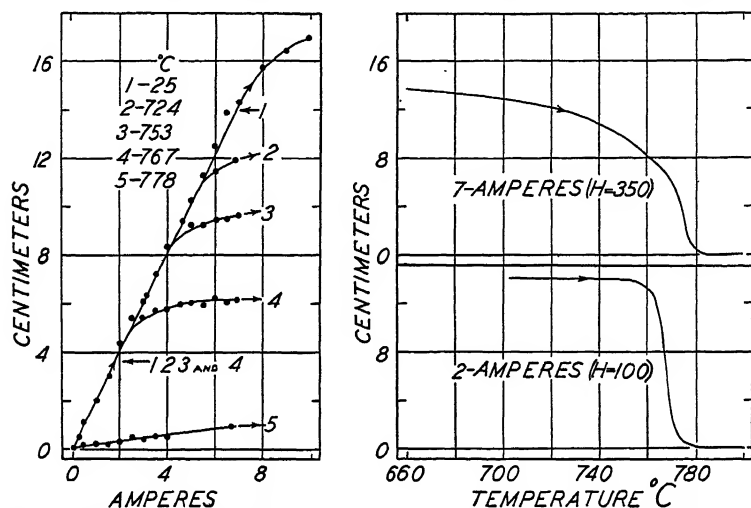


FIG. 29.—ISOTHERMAL MAGNETIC FLUX-MAGNETIZING FORCE AND THERMOMAGNETIC CURVES, HIGH-PURITY IRON.

Showing effect of  $H$  (magnetizing force) on degree of magnetic saturation at various temperatures and on shape of thermomagnetic curves. Centimeters are proportional to magnetic flux.

the same shape and show the same value for the temperature at which the magnetism has practically disappeared, despite the fact that the curves at lower temperatures are quite different in shape, owing to the difference of the magnetizing force.

The results of the thermomagnetic analysis showing the influence of carbon on the Curie temperature range and on the  $A_1$  transformation, respectively, are given in Fig. 30. The magnetizing force was about 100 gilberts per centimeter, and the heating and cooling rate  $2^{\circ}\text{C.}$  per minute. All the specimens were heated to and cooled from  $785^{\circ}\text{C.}$  and therefore, except for one alloy (0.55 per cent C), were not entirely transformed to the  $\gamma$ -iron-carbon solid solution before cooling. The magnetic change is reversible in the carbonyl iron (0.5 per cent oxygen, mostly oxide), the

\* Scale readings in centimeters are proportional to the magnetic flux of the specimen, and the magnetizing coil current is proportional to the magnetizing force  $H$ .



hydrogen-treated carbonyl iron, and the electrolytic iron (0.012 per cent C) (Fig. 30). The  $Ac_1$  and  $Ar_1$  temperatures were not determined thermomagnetically for all the alloys noted in Fig. 30, but those deter-

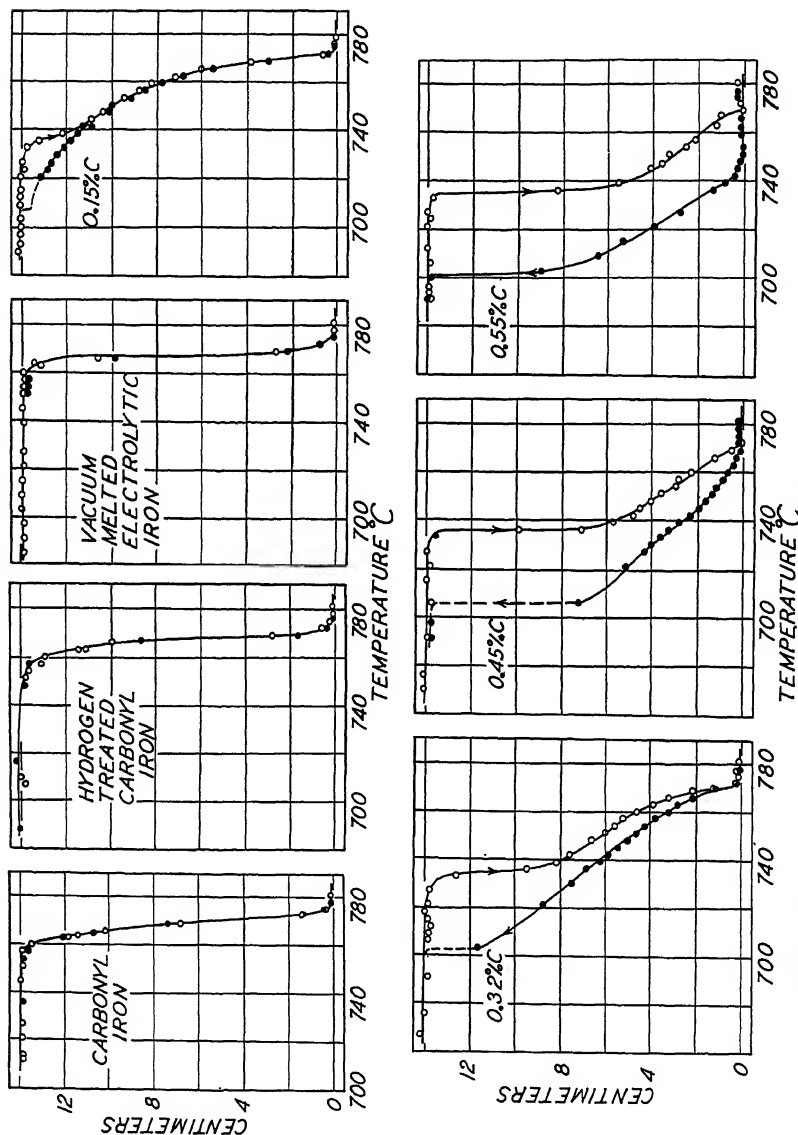


Fig. 30.—THERMOMAGNETIC CURVES SHOWING INFLUENCE OF CARBON ON MAGNETIC BEHAVIOR OF IRON-CARBON ALLOYS. Rate of heating and cooling,  $2^{\circ}\text{C}$ . per minute. Magnetizing force used was 100 gilberts per centimeter.

mined agree with those obtained by dilatometric methods (see Fig. 9) and show that the phase and electronic changes take place simultaneously. The  $Ac_2$  transformation temperatures in alloys with 0.15 to 0.45 per cent

C, when heated at  $2^{\circ}$  C. per minute, are above the Curie point temperatures and therefore cannot be determined thermomagnetically.

The results of the thermomagnetic studies (alloys up to 0.45 per cent C) show that the disappearance of magnetism at  $775^{\circ}$  C. on heating and reappearance on cooling at  $775^{\circ}$  C. mark the end of the Curie magnetic transformation on heating and the beginning on cooling; but the results give no indication of  $Ac_3$  and  $Ar_3$  transformations. In none of these tests was the  $\alpha$ -iron completely transformed to  $\gamma$ -iron, and for this reason the

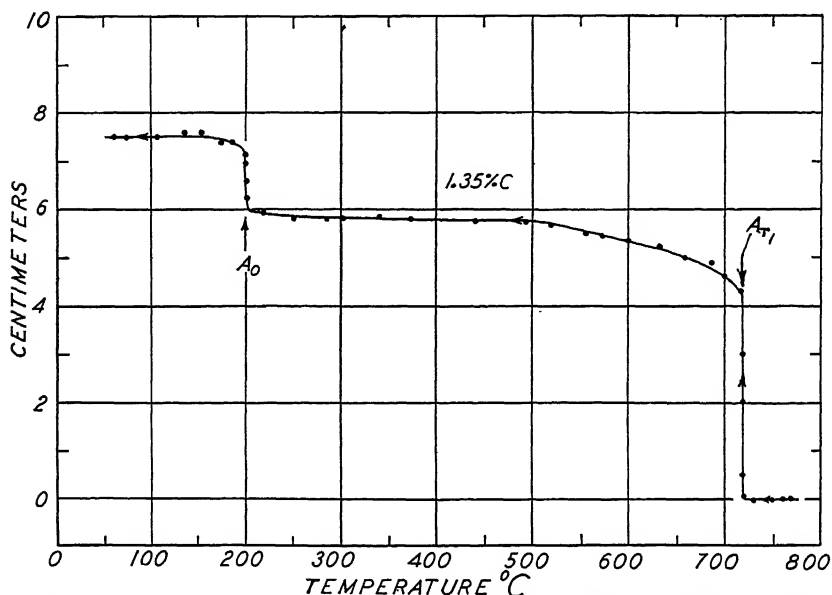


FIG. 31.—THERMOMAGNETIC COOLING CURVE SHOWING  $Ar_1$  AND  $A_0$  TEMPERATURES IN A 1.35 PER CENT C ALLOY.

Rate of cooling,  $2^{\circ}$  C. per minute. Centimeters are proportional to magnetic flux.  $H$  (magnetizing field) 350 gilberts per centimeter.

end of the magnetic transformation on heating and the beginning on cooling are coincident.

The thermomagnetic curves for the 0.55 per cent C alloy, Fig. 30, taken at a rate of heating and cooling of  $2^{\circ}$  C. per minute show that the partial loss of magnetism at the  $Ac_1$  and  $Ar_1$  temperatures occurs over a very small range of temperatures; namely, less than  $3^{\circ}$  C. The reappearance of magnetism on cooling occurred at a temperature somewhat higher than might have been obtained if the alloy had been heated to a higher temperature above the  $Ac_3$  point and thus been rendered more homogeneous.

The thermomagnetic study of the 0.77 per cent C alloy heated and cooled at a  $2^{\circ}$  rate (Fig. 9, curve A) gives an  $Ac_3$  temperature of  $740^{\circ}$

which is the temperature to be predicted from the diagram (Fig. 33). This temperature is considerably below the Curie point of iron.

Fig. 31 shows the results of the thermomagnetic study of the  $A_0$  magnetic point in  $\text{Fe}_3\text{C}$  and of the  $A_{r1}$  point in an alloy with 1.35 per cent C. The  $A_0$  point in  $\text{Fe}_3\text{C}$ , like the  $A_2$  point in iron and iron alloys, is entirely reversible.

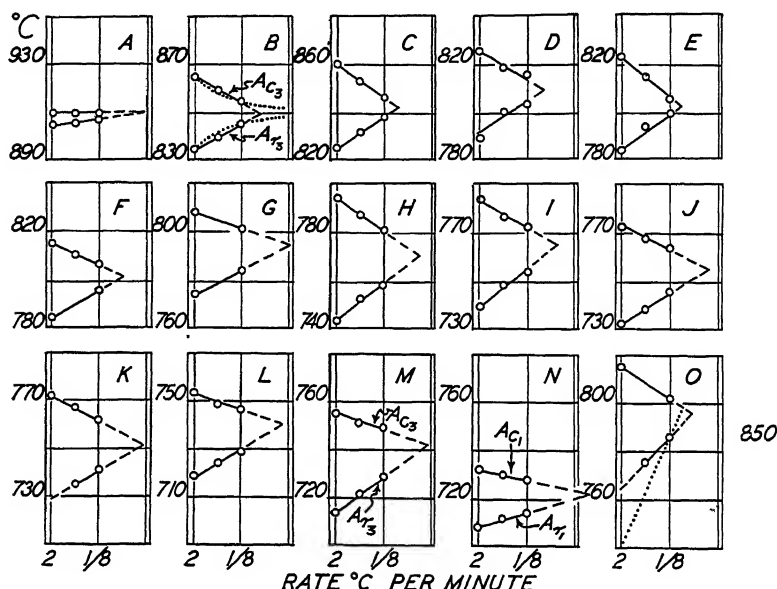


FIG. 32.—ILLUSTRATING METHOD OF EXTRAPOLATION USED TO DETERMINE THE  $A_3$  AND  $A_1$  TEMPERATURES FROM  $Ac_3$ ,  $Ar_3$  AND  $Ac_1$ ,  $Ar_1$  DATA.

Showing influence of rate of heating and cooling on  $A_3$  and  $A_1$  temperatures. Samples as follows:

A, hydrogen-purified carbonyl iron.

PER CENT C

B, 0.135

E, 0.302

H, 0.458

K, 0.579

N, 0.310

PER CENT C

C, 0.160

F, 0.310

I, 0.487

L, 0.663

O, 0.972

PER CENT C

D, 0.280

G, 0.341

J, 0.544

M, 0.665

### Microscopic Results

Microscopic results are given in Table 5, and no further discussion of them is necessary.

### Results of the Four Methods

The results of each of the four methods of investigation used in this work are presented as follows: (1) dilatometric results in Figs. 15, 17 to 22, 32, 45, in Table 4, and in the diagrams Figs. 33 to 35 and Fig. 43; (2) thermal results in Figs. 9 and 20;\* (3) magnetic results in Figs. 9, 29 to

\*  $Ac_1$  and  $Ar_1$  thermal data were obtained for all the alloys listed in Table 4 when rates of  $2^\circ$  and  $\frac{1}{2}^\circ$  C. were used for heating and cooling. These in every case agreed with the dilatometric data given in this table within  $\pm 1^\circ$  C.

31; and (4) results of microscopic studies in Figs. 2 to 6, 10 to 13, 16, 23 to 28, 36 to 42, in Table 5, and in the diagram of Fig. 43.

TABLE 4.—*Dilatometric Data*

Transformation		Ac <sub>3</sub>			Ar <sub>3</sub>			A <sub>3</sub>	Ac <sub>1</sub>			Ar <sub>1</sub>			A <sub>1</sub>
Heating and Cooling Rates, Deg. C. per Minute		2	½	⅛	2	½	⅛	0	2	½	⅛	2	½	⅛	0
Alloy No.	Weight Per Cent Carbon														
F3	0.135	865	859	855	834	840	845	849	732	730	729	704	706	708	720
F41	0.160	860	853	846	825	832	838	842	735		730	709	710	713	722
F41'	0.160											707			
F20	0.280	825	818	815	788	800	803	809	732			707			
F20'	0.280	826			789										
F4*	0.302	823	814	805	784	793	799	802	731			708			
F4'	0.302								731						
F19	0.310	816	810	806	784		796	801	732	730	728	708	711	714	722
F19'	0.310	817			786										
F12	0.341	808		801	774		784	795	730	728	726	708	713	713	721
F40	0.458	794	787	781	743	752	758	770							
F40'	0.458				743										
F44	0.487	787	778	772	739	749	754	765	733	731	730	709	713	716	724
F44'	0.487	785			736				732			710			
F39	0.544	772	768	764	732	738	745	755	733	733	729	710	712	716	723
F39'	0.544	774			733										
F29	0.579	772	767	762		735	741	752							
F29'	0.579	773													
F30	0.663		749	747	719	724	729	741	734	732	729	711	715	717	724
F31	0.665		752	749	714	722	728	742	732	730	729	710	713	717	724
F31'	0.665		749	747		724	729				729				
F32	0.77								734	731	730	707	712	715	723
F32'	0.77											707			
F45	0.972	815		802		775	786	796	734	731		714	717	718	724
F45'	0.972	815													

\* For sample F4 the temperature gradient in the specimen was not carefully controlled; the temperatures quoted are good to within  $\pm 3^\circ$ .

For all other specimens the lengthwise temperature gradient in the sample was kept within  $\frac{1}{2}^\circ$  in the vicinity of the transformation temperatures. The data taken at  $2^\circ$  per minute are good to within  $\pm 2^\circ$ ; those at  $\frac{1}{8}^\circ$  per minute, to within  $\pm 1^\circ$ .

### DISCUSSION OF RESULTS

Various methods have been used in plotting dilatometric data, as stated in the introduction. Sato<sup>5</sup> plotted critical temperatures against rates of heating and cooling. Yap<sup>7</sup> plotted Sato's data with logarithmic scales for both critical temperatures and rates. Upton<sup>6</sup> plotted the critical temperatures against the cube root of the rates, and Austin<sup>12</sup> plotted the critical temperatures against the fourth-power root of the



side and of cooling to the other, and thus not permitting easy graphical extrapolation. Upton believes that the amounts of superheating and supercooling are nearly proportional to the cube root of the rates, so that straight lines are obtained when transformation temperatures are plotted against the cube root of the rates; Austin, however, thinks the fourth power may be equally well substituted for the cube root in the above plot.

In this investigation the superheating and undercooling data have been plotted using all of the methods suggested. The method finally

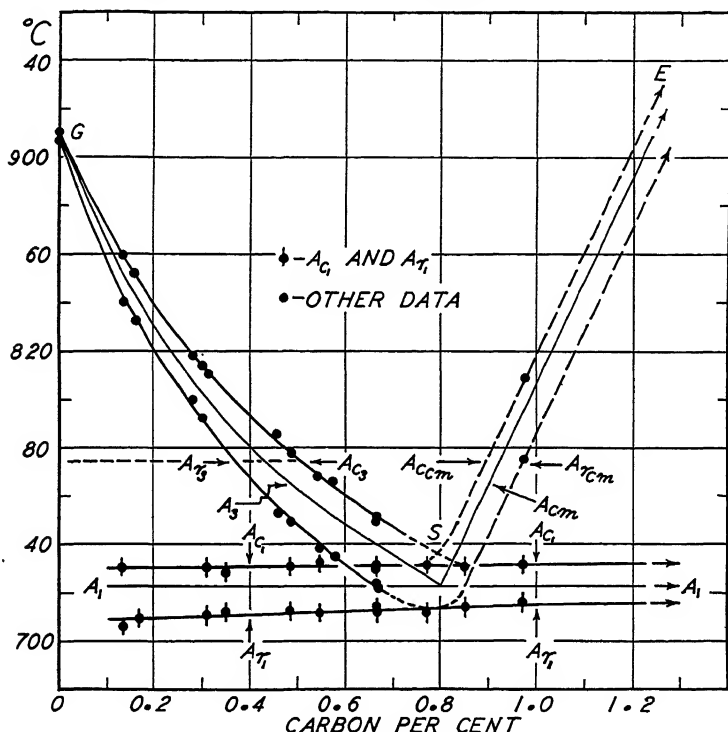


FIG. 34.—IRON-IRON CARBIDE DIAGRAM SHOWING EFFECT OF CARBON CONTENT ON DEGREE OF SUPERHEATING AND UNDERCOOLING OF  $A_3$  AND  $A_1$  TRANSFORMATIONS AT RATES OF HEATING AND COOLING OF  $\frac{1}{2}^\circ$  C. PER MINUTE.

adopted as the most useful consisted in a simple plot of the logarithm of the rate of heating or cooling against the temperature, and a linear extrapolation of the observed temperatures to the point of intersection of the curves (Fig. 32). This point of intersection must not be interpreted as representing a finite rate at which true equilibrium is attained, but merely as a convenient point of extrapolation; obviously the curves will approach the horizontal equilibrium temperature asymptotically, somewhat as shown in the dotted curves with curves B. This method and those itemized above all give the same extrapolated equilibrium temperature within  $1^\circ$ .

The influence of the rates of heating and of cooling on the  $Ac_3$  and the  $Ar_3$  temperatures for alloys between zero and 0.70 per cent C are given in curves A to M in Fig. 32.\*

The addition of only 0.135 per cent C to iron very markedly changes the influence of rate, as shown by curves A and B. For alloys between 0.1 and 0.7 per cent C, the slopes of the superheating and supercooling curves are practically the same within experimental error. Also, the

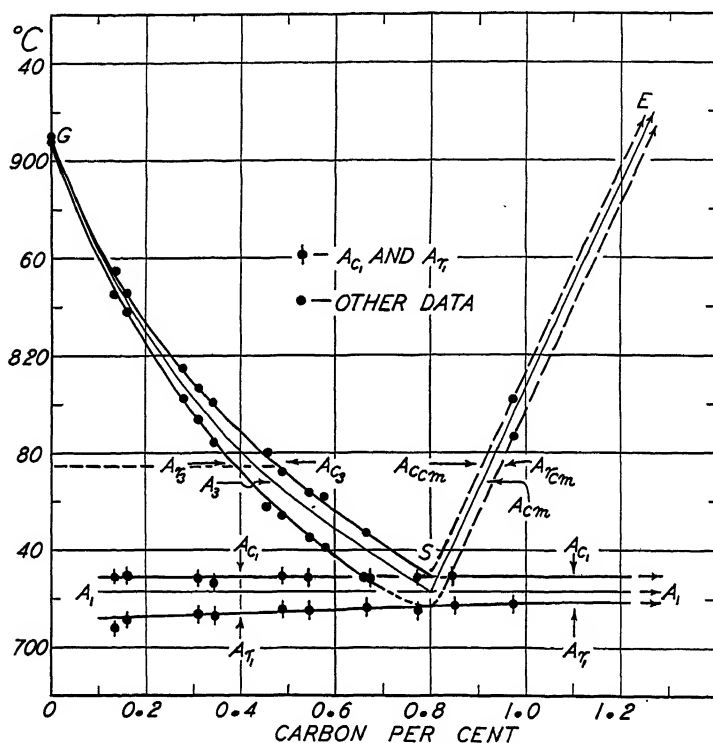


FIG. 35.—IRON-IRON CARBIDE DIAGRAM SHOWING EFFECT OF CARBON CONTENT ON DEGREE OF SUPERHEATING AND UNDERCOOLING OF  $A_3$  AND  $A_1$  TRANSFORMATIONS AT RATES OF HEATING AND COOLING OF  $\frac{1}{8}^{\circ}$  C. PER MINUTE.

separation of the curves tends to increase with increasing carbon content and the points of intersection are removed farther to the right; i.e., longer times are required to reach equilibrium. This latter fact is readily understood, for greater time is required in the higher carbon alloys for the diffusion of the greater amounts of carbon, and in addition the transformation temperatures are lower and therefore the rate of diffusion of carbon is slower.

The slope of the  $Ac_1$  and the  $Ar_1$  curves is much less than for the  $Ac_3$  and the  $Ar_3$  curves (see curve N, Fig. 32) and a much longer time is

\* The austenitic grain sizes in these alloys have been given in Table 3.

required to reach equilibrium, for the point of intersection of these curves is far to the right.

Curve *O* in Fig. 32 is shown to represent the effect of rates of heating and cooling on the  $A_{cm}$  temperature. The  $A_{cm}$  temperature obtained by extrapolation, namely  $796^{\circ}$ , agrees quite well with that determined microscopically, namely  $797^{\circ}$ . Although the dilatometric results on hypereutectoid alloys are not particularly useful in determining the  $A_{cm}$  temperature, a considerable difference in slope in the  $Ar_{cm}$  curve makes but little difference in the extrapolated point ( $\pm 2^{\circ}$ , or 0.005 per cent C); this is shown by comparison of the dotted  $Ar_{cm}$  with the full  $Ar_{cm}$  curve in *O*, Fig. 32.

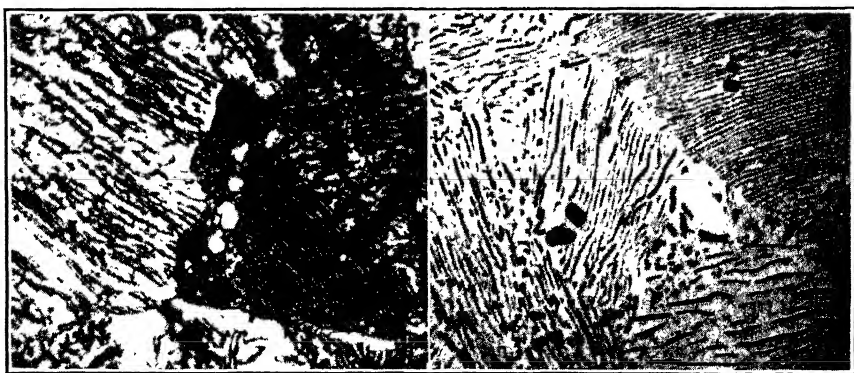


FIG. 36.

FIG. 37.

FIG. 36.—ALLOY 0.78 PER CENT C. SHOWS CARBIDES (SPHEROIDAL) UNDISSOLVED AT  $733^{\circ}$  C.

Heated 3 hr. at  $733^{\circ}$  C. (above  $Ac_1$ ) and cooled at about  $50^{\circ}$  C. per minute. Etched with nital.

FIG. 37.—ALLOY 0.78 PER CENT C. SHOWS CARBIDES (BLACK SPHEROIDS) UNDISSOLVED AT  $733^{\circ}$  C.

Heated 3 hr. at  $733^{\circ}$  C. and cooled at about  $50^{\circ}$  C. per minute. Etched with sodium picrate.

Original magnification 2000; reduced  $\frac{1}{4}$  in reproduction.

Figs. 33, 34 and 35 show the influence of carbon content on the degree of superheating and of undercooling. The data have been determined with sufficient accuracy and on a sufficient number of alloys to furnish curves of this sort with an accuracy of  $\pm 2^{\circ}$  for the  $2^{\circ}$  rate and  $\pm 1^{\circ}$  for the  $\frac{1}{8}^{\circ}$  rate.

The dilatometric data on hypereutectoid alloys are too meager to be of much use in fixing the  $Ar_{cm}$  and  $Ac_{cm}$  lines; those given are accurate within about  $\pm 5^{\circ}$ .

The diagrams are for the most part self-explanatory, though some special mention must be made on the construction of the diagram near the eutectoid point *S*, for rates of heating and of cooling of  $2^{\circ}$  per minute. If in Fig. 33 the  $Ac_3$  and  $Ac_{cm}$  lines were prolonged they would intersect at point *S*. The thermomagnetic analyses of the alloys with 0.77 and



0.78 per cent C (Fig. 9, curve A) showed ferrite to persist up to  $740^{\circ}\text{C.}$  at a rate of heating of  $2^{\circ}$  per minute; the microscopic studies of these alloys, on the other hand, show the presence of carbides in these alloys after heating at  $733^{\circ}$  for  $3\frac{1}{2}$  hr., as shown in Figs. 36 and 37. Evidently, the heterogeneity originating in the initial cooling persisted on reheating above the  $A_{c1}$  temperature, thus giving both carbide and ferrite above this temperature; the degree of persistence of these phases is surprising. In connection with the  $A_{r3}$  and  $A_{r_{cm}}$  points in the vicinity of the eutectoid composition it should be noted that the  $A_{r1}$  arrest has its maximum value

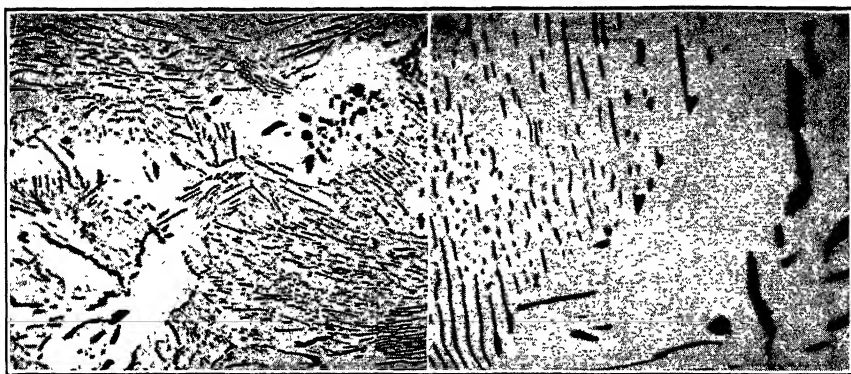


FIG. 38.

FIG. 39.

FIG. 38.—ALLOY 0.74 PER CENT C. COOLED FROM  $740^{\circ}\text{C.}$  AT  $\frac{1}{8}^{\circ}\text{C.}$  PER MINUTE. SHOWS CONSIDERABLE PROEUTECTOID FERRITE PRECIPITATED IN ALLOY DURING COOLING.

Etched with sodium picrate. Original magnification 250; reduced  $\frac{1}{4}$  in reproduction.

FIG. 39.—ALLOY 0.74 PER CENT C. COOLED FROM  $740^{\circ}\text{C.}$  AT  $\frac{1}{4}^{\circ}\text{C.}$  PER MINUTE. SHOWS CONSIDERABLE PROEUTECTOID FERRITE FORMED DURING COOLING.

Etched with sodium picrate. Original magnification 1500; reduced  $\frac{1}{4}$  in reproduction.

in these alloys and that the temperature arrest so much retards the rate of heating that time is available for the formation of a greater amount of austenite; i.e., less apparent superheating occurs, and accordingly the  $A_{r3}$  and  $A_{r_{cm}}$  curves have a downward dip in the vicinity of the eutectoid composition.

The dilatometric studies performed at rates of cooling of  $2^{\circ}$  per minute on alloys containing between 0.70 and 0.90 per cent C furnish little evidence for the occurrence of  $A_{r3}$  and  $A_{r_{cm}}$  points, owing to the very small amounts of ferrite formed at this rapid rate of cooling in hypoeutectoid and of carbide in hypereutectoid alloys before the  $A_{r1}$  temperature is attained. At slower rates of cooling this range was decreased to 0.75 to 0.85 per cent C. In an alloy with 0.74 per cent C cooled at  $2^{\circ}$  per minute, very little evidence appeared on the dilatometric curve for an  $A_{r3}$  temperature, but this temperature was quite clearly indicated when the

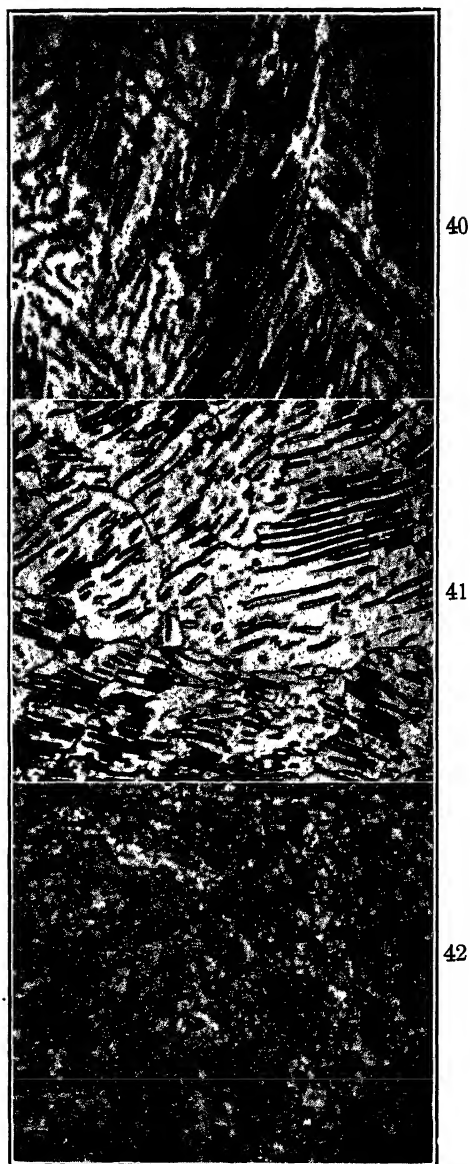


FIG. 40.—ALLOY 0.77 PER CENT C. COOLED FROM  $885^{\circ}$  C. AT  $2^{\circ}$  C. PER MINUTE.  
SHOWS LAMINAR PEARLITE FORMED DURING COOLING.

FIG. 41.—ALLOY 0.77 PER CENT C. COOLED FROM  $885^{\circ}$  C. AT  $\frac{1}{2}^{\circ}$  C. PER MINUTE.  
SHOWS LAMINAR PEARLITE WITH A TENDENCY TOWARD SPHEROIDIZATION.

FIG. 42.—ALLOY 0.77 PER CENT C. COOLED FROM  $885^{\circ}$  C. AT  $\frac{1}{8}^{\circ}$  C. PER MINUTE.  
SHOWS SPHEROIDIZED PEARLITE FORMED DURING COOLING.

Etched with nital. Original magnification 1500; reduced  $\frac{1}{4}$  in reproduction.

specimen was cooled at  $\frac{1}{8}^{\circ}$  per minute. Figs. 38 and 39 show the amount of proeutectoid ferrite formed in the latter case.

Upton<sup>6</sup> concluded from his studies of Sato's data that the relatively greater extent of undercooling of the  $Ac_3$  and  $Ac_{cm}$  temperatures in comparison to that of the  $A_1$  temperature implied that the  $Ar_3$  and the  $Ar_{cm}$  lines should intersect the  $Ar_1$  line not at a single point, as in an equilibrium diagram, but at points separated by a finite carbon range, so that alloys within this range should all be completely pearlitic. Sato used very fast rates of cooling, and owing to the fineness of the division of proeutectoid ferrite and pearlite resulting from such treatment, it is difficult to recog-

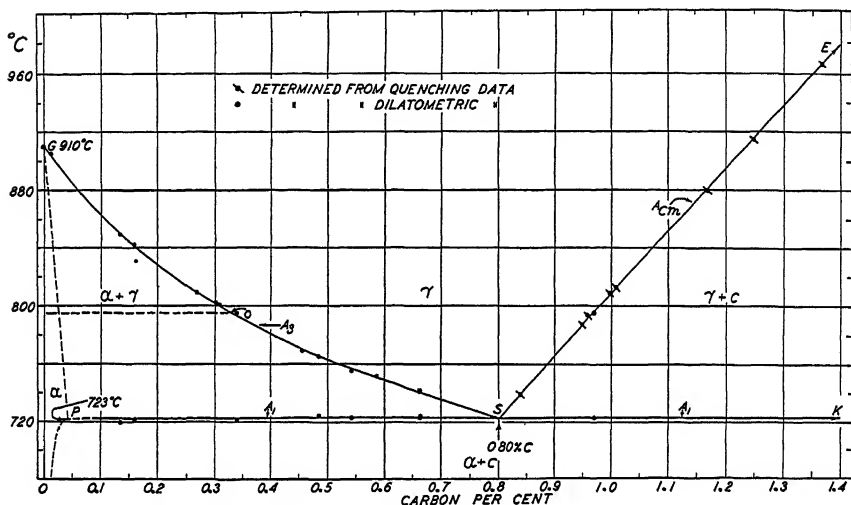


FIG. 43.—IRON-IRON CARBIDE CONSTITUTIONAL DIAGRAM.

nize the proeutectoid ferrite in the microstructure. A correlation of the dilatometric and the microscopic data obtained in the present study does not support Upton's point of view. Proeutectoid ferrite was found to be present even when the dilatometer gave no evidence of the presence of an  $Ar_3$  point (Fig. 21, curve  $E$ ; Fig. 40), owing to its close proximity to the  $Ar_1$  temperature. Similar results were obtained for hypereutectoid alloys. Evidently the  $Ar_3$  and  $Ar_{cm}$  curves become nearly tangent to the  $Ar_1$  curve in the neighborhood of the eutectoid composition at the rates of cooling used.

A correlation of the dilatometric results (Fig. 21) with the microscopic results (Figs. 25 and 26) on a 0.665 per cent C alloy showed that considerable proeutectoid ferrite may separate both at the austenite grain boundaries and within the grain without much evidence for the reaction appearing on the dilatometric curves. The dilatometric studies suggest that much of this proeutectoid ferrite separates at the eutectoid temperature; following this—as judged from the microstructure—primary

cementite forms in relatively large masses, and the remaining austenite then transforms bodily to lamellar pearlite.

The  $A_{c1}$  temperatures are constant over the full carbon range, whereas the  $A_{r1}$  temperatures are lower in the lower carbon alloys<sup>5</sup>. This may be restated: the residual austenite in low-carbon steels supercools to a greater extent than in high-carbon steels (Figs. 33, 34 and 35). The reason for this is not clear; Sato<sup>5</sup> advanced an explanation, which is difficult to understand. Figs. 23 and 24 show very large carbide masses with no detectable pearlite in Fig. 23 and only a small amount in Fig. 24. It is

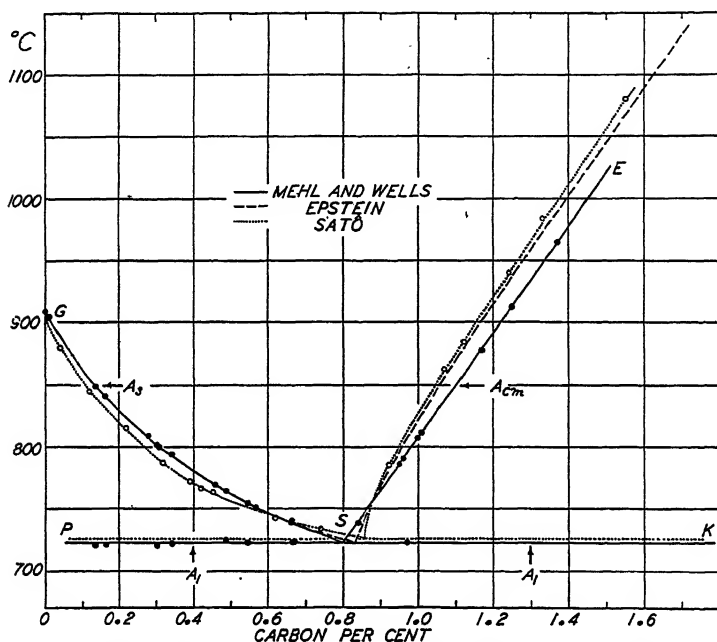


FIG. 44.—IRON-IRON CARBIDE CONSTITUTIONAL DIAGRAM AS DETERMINED BY MEHL AND WELLS, AND SATO AND FROM DATA SELECTED BY EPSTEIN.

possible that this structure originates in a rapid rate of spheroidization of the pearlite during its formation, but the angular outlines of the carbide masses suggest that the carbide is proeutectoid; it is possible that the great preponderance of ferrite at the  $A_1$  temperature exercises a powerful inoculating effect on the residual austenite leading to an excess formation of ferrite, and that the resulting state of supersaturation in the austenite with respect to carbon thus leads to the precipitation of proeutectoid carbide before the true pearlite reaction can take place. Figs. 40, 41 and 42 show the influence of the rate of cooling on the appearance of pearlite. At a rate of  $2^\circ$  per minute the pearlite is mostly lamellar (Fig. 40), at a rate of  $\frac{1}{2}^\circ$  per minute both lamellar and spheroidized (Fig. 41), and at a rate of  $\frac{1}{8}^\circ$  per minute practically completely spheroidized (Fig. 42).

Fig. 43 gives the  $A_3$ ,  $A_{cm}$  and the  $A_1$  lines determined with an accuracy of  $\pm 2^\circ$ . The difference between the plotted points and the smooth curve lies between  $0^\circ$  and  $3^\circ$ , amounting to  $1^\circ$  in most cases. The greatest difference,  $3^\circ$ , is for the  $A_1$  temperature for the alloy with 0.135 per cent C; this is not surprising for, as already noted, it is very difficult to determine

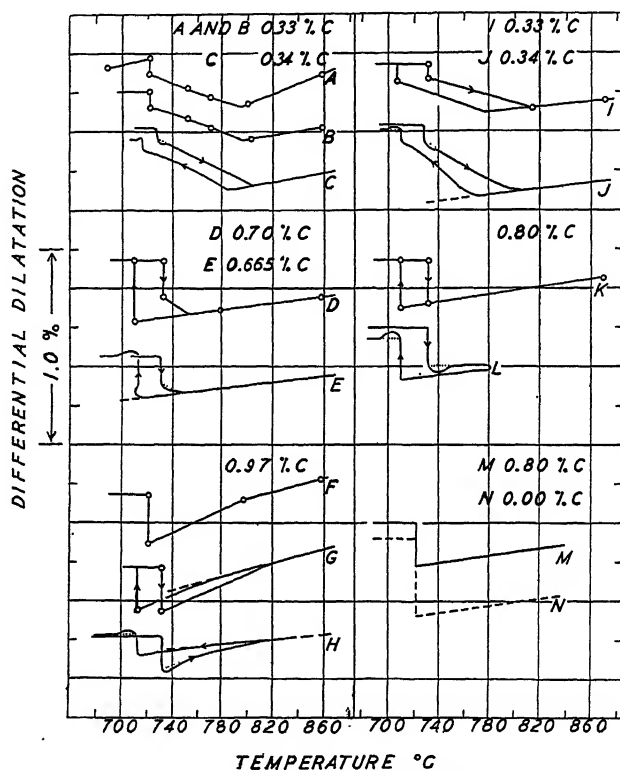


FIG. 45.—CALCULATED AND EXPERIMENTALLY DETERMINED DILATOMETRIC CURVES.

Curve A. Dilatometric curve calculated from X-ray data and diagram Fig. 43.

Curves B, F, M, N. Differential dilatometric curves calculated from X-ray data and diagram Fig. 43.

Curves D, G, I, K. Differential dilatometric curves calculated from X-ray data and diagram Fig. 33.

Curve C. Experimentally determined differential dilatometric curve. Heating and cooling rate:  $\frac{1}{8}^\circ$  C. per minute.

Curves E, H, J, L. Experimentally determined differential dilatometric curves. Heating and cooling rate:  $2^\circ$  C. per minute.

the  $A_1$  temperatures in very low-carbon alloys. It will be noted that the dilatometric data for the  $A_{cm}$  line agrees well with the microscopic. This shows that the annealing periods used in the microscopic studies (Table 5) were adequate. No effort has been made to determine the solvus curve of the solubility of C in  $\alpha$ -iron. The  $A_1$  temperatures are constant between 0.16 and 0.97 per cent C to within  $\pm 1^\circ$ . The  $A_1$  temperature

given is  $723^{\circ}$ , and the eutectoid composition is 0.80 per cent C, which is probably correct to within  $\pm 0.01$  per cent C.

The  $A_3$ ,  $A_{cm}$  and  $A_1$  temperatures obtained by Sato<sup>5</sup> and those selected by Epstein<sup>2</sup> are given in Fig. 44, together with the data obtained in the present work. The points of similarity and of disagreement may readily be seen; Epstein's  $A_3$  curve and  $A_1$  curve coincide with those determined here. The high  $A_{cm}$  temperatures given by Sato doubtless were caused by the high silicon content of his alloys.

The results of magnetic analyses are in general agreement with those of Esser<sup>4</sup> and Sato<sup>5</sup> and show that the Curie point in iron is about  $775^{\circ}$  C. This temperature, at which the Curie magnetic transformation is complete, is not appreciably affected by carbon content until such a carbon concentration is reached that the  $Ac_3$  transformation on heating or the  $Ar_3$  on cooling occurs below  $775^{\circ}$ . A magnetic change is associated with the  $Ac_1$  and  $Ar_1$  transformations, owing to the change in the amount of ferromagnetic ferrite. The magnetic changes at  $A_1$  were the only ones in hypereutectoid alloys at high temperatures except the small changes noted which occurred above the  $Ac_1$  temperature on heating and were undoubtedly caused by heterogeneity. The  $A_0$  temperature, the temperature of the magnetic change in cementite, namely  $200^{\circ}$ , is also in agreement with previous results, though it had not been shown previously that the  $A_0$  transformation takes place entirely at constant temperature. This transformation, like the Curie transformation, is reversible.

Calculations have been made of ideal dilatometric curves using the Fe-Fe<sub>3</sub>C diagram shown in Fig. 43 and the curves of lattice parameter versus carbon composition at different temperatures (in order to obtain data on volume) as determined by Esser and Mueller<sup>13</sup>. In making these calculations the solubility of carbon in  $\alpha$ -iron was assumed to be 0.04 per cent at  $A_1$  decreasing linearly to  $A_3$ ; the density of Fe<sub>3</sub>C was taken to be 7.62, and that of  $\alpha$ -iron 7.885. These densities were converted to volumes at  $723^{\circ}$  under the assumption that the temperature coefficients of expansion are approximately the same. Thus the volumes just below  $A_1$  for an alloy of any carbon content could be calculated, and compared to that above the  $A_1$  temperature calculated with these data and the volume of austenite as determined from the data of Griess and Esser. This method was followed throughout the transformation range. In calculating differential dilatometric curves it was assumed that the comparison piece was pure  $\alpha$ -iron. These calculated curves are given in Fig. 45 with calculated points plotted as hollow circles. Experimentally determined curves are given for comparison, shown by full lines.

Curves *D*, *G*, *I* and *K* are calculated curves drawn to represent true length (volume) changes at a rate of heating and cooling of  $2^{\circ}$  per minute; these were obtained by taking the  $Ar_1$  and  $Ac_1$  and the  $Ar_3$  and  $Ac_3$  temperatures from the experimental curves and then calculating volumes

and finally lengths. Curve  $N$  is a theoretical curve for pure iron calculated on the assumption that the  $A_3$  transformation takes place at the eutectoid temperature; it is introduced together with a calculated curve for a eutectoid steel to show a comparison of the volume changes.

### SUMMARY

1. A series of approximately 60 high-purity iron-carbon alloys has been prepared in the carbon range  $0^\circ$  to 1.4 per cent C. The alloys were made from hydrogen-purified carbonyl iron by gas carburization in mixtures of dipentene-hydrogen and dipentene-benzene-hydrogen. The technique for preparing homogeneous alloys of any desired carbon content is described. Spectroscopic and chemical analyses showed these alloys to be of very high purity.

2. The  $Ar_3$  and  $Ac_3$ , the  $Ar_1$  and  $Ac_1$ , and the  $Ac_{cm}$  and  $Ar_{cm}$  temperatures in these alloys were determined by the dilatometric, the thermal analytical, the magnetic and the microscopic methods. For the first two methods constant rates of heating and cooling of  $2^\circ$ ,  $\frac{1}{2}^\circ$  and  $\frac{1}{8}^\circ$  per minute were employed. The data thus give information on the degrees of superheating and undercooling in the metastable Fe-Fe<sub>3</sub>C system.

3. The dilatometric behavior of these alloys is discussed in detail; the transformation temperatures determined dilatometrically are accurate to  $\pm 1^\circ$  C. at the slowest rate. The effect of carbon content on the degrees of superheating and supercooling is discussed. The dilatometric evidence for  $A_3$  or  $A_{cm}$  transformations at rates of  $2^\circ$  per minute in alloys between 0.7 and 0.9 per cent C was slight and somewhat questionable, but microscopic studies showed the presence of proeutectoid ferrite and cementite. The dilatometer is not particularly useful in determining the  $A_{cm}$  temperatures in alloys with less than 1 per cent C, for the volume changes are not sufficiently sharply indicated on the dilatometric curves.

4. No evidence was found of the Curie point, the  $A_2$  temperature, in the austenite field; up to the point where the Curie temperature coincides with the  $A_3$  temperature, the temperature at which the alloys wholly lose their magnetism is  $775^\circ$  C. The  $A_0$  point in Fe<sub>3</sub>C is at  $200^\circ$  C.

5. The extrapolation of the dilatometrically determined transformation-temperature data to zero rates of heating or cooling is discussed. The data presented for the  $A_3$  and  $A_1$  temperatures have been extrapolated and the equilibrium curves drawn. These are believed to be accurate to  $\pm 2^\circ$  C.

6. The microscopically determined  $A_{cm}$  curve is accurate to about  $\pm 3^\circ$  C.

7. The eutectoid composition is  $0.80 \pm 0.01$  per cent C; the  $A_1$  temperature is  $723^\circ \pm 2^\circ$  C.

8. Ideal dilatometric curves have been calculated from density data and compared with the experimental curves and the reasons for deviations discussed.

#### ACKNOWLEDGMENT

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#### DISCUSSION

(F. T. Sisco presiding)

J. B. AUSTIN,\* Kearny, N. J. (written discussion).—Some time ago, the authors of this paper sent us samples of four of their high-purity iron-carbon alloys to be used in a study of the influence of carbon on the thermal-expansion coefficient of iron. As

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our investigation was carried to temperatures above the transformation, we obtained measurements of the  $A_1$  and  $A_2$  temperatures of the alloys as a by-product, and in so far as they are comparable, our results are in excellent agreement with those of Mehl and Wells.

At the suggestion of Dr. Wells, the alloys were homogenized before the carbon content was determined, by sealing the samples in silica tubes and giving them a treatment of 14 hr. at  $1050^\circ\text{C}$ . The thermal-expansion measurements were made in our vacuum interferometer using a rate of heating of  $3^\circ\text{C}$ . per minute. An attempt was made to cool at the same rate but in our dilatometer the rate of cooling is more difficult to control than the rate of heating, so that the cooling was sometimes faster than the  $3^\circ\text{C}$ . a minute desired. Duplicate heating and cooling runs were made on each alloy.

The most rapid rate of heating and cooling used by Mehl and Wells was  $2^\circ\text{C}$ . a minute; so that our data are not strictly comparable with theirs; nevertheless, since the difference between  $2^\circ$  and  $3^\circ\text{C}$ . a minute is not large, we have made a comparison, keeping in mind that perfect agreement is not to be expected.

Of our eight determinations of the  $Ac_1$  temperatures all fell within the range  $730^\circ$  to  $732^\circ\text{C}$ ., in excellent agreement with the values given by Mehl and Wells in Table 4, which lie within the range  $730^\circ$  to  $735^\circ\text{C}$ . Six of our eight determinations of the  $Ar_1$  temperature lay between  $688^\circ$  and  $695^\circ\text{C}$ ., which is appreciably lower than the range  $704^\circ$  to  $711^\circ\text{C}$ . given in Table 4, but the difference is almost certainly due to the fact that our cooling rates were somewhat faster than  $3^\circ\text{C}$ . per minute.

In comparing the  $Ac_2$  and  $Ar_2$  temperatures, it is not possible to use the numerical values given by Mehl and Wells in their table, because measurements are not reported for alloys of the same carbon content as those we used; consequently, it is necessary to compare our observations with the  $A_2$  temperatures corresponding to the composition of our alloys as read from Fig. 33. This comparison, made in Table 6, shows that, on the whole, the agreement is remarkably good.

I should like to venture the prediction that this paper will take its place among the classics of ferrous metallurgy because it marks the first time that equilibrium relations

TABLE 6.—*Comparison of  $Ac_2$  and  $Ar_2$  Temperatures with Those Given by Mehl and Wells*

Alloy No.	Carbon Content, Weight Per Cent	$Ac_2$ Temperature, Deg. C.		$Ar_2$ Temperature, Deg. C.	
		Mehl and Wells Fig. 33	At $3^\circ\text{C}$ . per Min.	Mehl and Wells Fig. 33	At $3^\circ\text{C}$ . per Min.
F41	0.222	840	$\begin{cases} 840 \\ 845 \end{cases}$	800	802
F5	0.312	816	$\begin{cases} 815 \\ 813 \end{cases}$	778	$\begin{cases} 774 \\ 779 \end{cases}$
F13	0.362	805	$\begin{cases} 817 \\ 806 \end{cases}$	765	$\begin{cases} 764 \\ 763 \end{cases}$
F30	0.674	755	$\begin{cases} 755 \\ 756 \end{cases}$	715	$\begin{cases} 713 \\ 712 \end{cases}$

in a binary ferrous system have been accurately established. After many years of research, the time has at last arrived when we are really justified in referring to the

eutectoid section of the diagram as given in Fig. 43 as *the* iron-carbon diagram; with this achievement ferrous metallurgy makes another strong claim to membership in the group of exact sciences.

J. G. THOMPSON,\* Washington, D. C.—I agree fully with what Dr. Austin has already said in regard to the value of the results obtained in this paper and to the way in which these results were obtained. One point that I think the authors would have been justified in spending considerably more time in describing was the method of carburizing and of handling their specimens, so that such beautiful uniform carburization was obtained. That phase is passed over as a mere detail, a preliminary detail, in the preparation of samples. As a matter of fact, anyone who has worked with carburizing at all will realize that the preparation of uniform carburized specimens and specimens with uniform structure is an achievement in itself.

F. T. SISCO,† New York, N. Y.—In the issue of *Metal Progress* for February, 1937, are reproduced the results of the work by the National Physical Laboratory on high-purity iron. As we all know, the  $A_3$  point of iron is of fundamental importance in the iron-carbon diagram. The  $A_3$  point used by Dr. Wells and that determined by the N.P.L. work are not in agreement. There is some  $35^\circ$ , I believe, between the two. What is the explanation of that discrepancy?

R. F. MEHL AND C. E. WELLS (written discussion).—The authors are pleased that Dr. Austin's results and theirs are in such remarkably good agreement. Dr. Thompson's comments are very welcome. In order to carburize iron in hydrogen-hydrocarbon mixtures as quickly as possible and obtain at the same time a uniform distribution of carbon, it is essential to use a high hydrogen-hydrocarbon ratio and a high temperature. As previously reported, in the footnote on page 431, Schenck has summarized the work on equilibria between hydrogen-methane mixtures and gamma iron, and it is seen that if one decides to use a temperature of carburization of  $1025^\circ\text{C}.$ , for example, and desires a homogeneous iron alloy containing 0.4 per cent, the gas mixture must contain a little less than 0.5 per cent of methane and a little more than 99.5 per cent of hydrogen, the partial pressure of the methane being of the order of 3.5 mm. Hydrogen was passed through various selected liquid hydrocarbons having approximately the above vapor pressure and the mixture was then used for carburizing purposes in the manner described in the paper. After using a number of such hydrocarbons in this way, dipentene, and later dipentene-benzene, mixtures were selected. Benzene is used with the dipentene in the preparation of the higher carbon alloys. It has two advantages—one, to increase first the hydrocarbon-hydrogen ratio; the other, to decrease it with time. This tends to give homogeneous alloys more quickly. In the preparation of the alloys benzene was not usually added during the last 12 hr. of the carburizing treatment.

The composition of the alloy prepared may be varied by changing the temperature of carburization, the temperature of the liquid hydrocarbons, the rate of the flow of the hydrogen-hydrocarbon mixtures through the carburizing furnace, and the time of carburization. In order to get as rapid homogenization as possible during the carburization process, and therefore limit the time required to obtain desired results, as high a carburizing temperature as possible should be used. The use of too high a temperature, however, will result in too rapid a decomposition of the hydrocarbons in the gas mixture and a deposition of carbon before the carburizing gases reach the specimen, resulting in a failure to obtain the desired carbon content in the alloy. This may be offset to some extent by increasing the rate of flow of the gases through the

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carburizing furnace. In general, however, in the preparation of the alloys referred to in this paper, the rate of flow of the gases (1 cu. ft. per hour) was not varied, and the carburizing temperature chosen was above 1000° and below 1200° C., especially in the preparation of hypoeutectoid alloys. The lowest temperature of the hydrocarbons used was 0° C. when making the lowest carbon content alloys, and the highest temperature was 35° C. when the alloys of highest carbon content were being made. If a temperature of more than 35° C. were used, liquid hydrocarbon would be deposited on the cooler parts of the apparatus and thereby change the composition of the carburizing gas mixture. In the preparation of the specimens of high-purity iron for carburization, the surfaces were ground and subsequently rubbed on No. 00 metallographic paper.

In answer to Mr. Sisco's question, the authors wish to first point out that the results of Adcock and Bristow,<sup>14</sup> to which he refers, do not indicate an  $\alpha$  to  $\gamma$  transformation at a single temperature, but over a temperature range of 26° C. on heating and 12° C. on cooling. In view of this fact, one cannot choose a particular temperature and claim that it represents accurately the  $A_3$  point in iron. Either one must accept the temperature range as being an inherent property of the iron or admit that the  $A_3$  transformation temperature was not accurately determined by Adcock and Bristow. Adcock and Bristow<sup>14</sup> themselves found it difficult to assign a reason for the discrepancy referred to by Mr. Sisco. They think that the  $A_3$  change in iron is complex and presumably causes the temperature range ( $\alpha \rightleftharpoons \gamma$ ) to exist in it, and that unknown factors may be operating. The possibility of a temperature gradient in specimens and of the carbon content (0.0045 per cent) affecting the results of Adcock and Bristow has been discussed previously.<sup>3</sup> In this respect those authors do not think that the gradient was larger than 2° or 3° C. However, be this as it may, Wells, Ackley, and Mehl<sup>3</sup> have shown definitely that 0.012 per cent carbon may cause a temperature spread at the  $\alpha$ - $\gamma$  transformation of as much as 34° C., so that the 0.0045 per cent carbon in Adcock and Bristow's alloys may cause a spread of several degrees. In the present investigation the  $A_3$  temperature was taken to be 910° C., because it has been determined accurately in iron of high purity, and the results have been confirmed in another laboratory. Furthermore, the  $A_3$  transformation in iron at 910° C. ( $\pm 1^\circ$  C.) has been observed to start and finish at one and only one temperature, and this is what one would normally expect to find in a single component system.

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<sup>14</sup> F. Adcock and C. A. Bristow: Iron of High Purity. *Proc. Roy. Soc.* (1935) 153, 172.

# X-ray Study on the Constitution of Iron-silicon Alloys Containing from 14 to 33.4 Per Cent Silicon

By EARL S. GREINER\* AND ERIC R. JETTE,† MEMBERS A.I.M.E.

(Cleveland Meeting, October, 1936)

THE constitution of the iron-silicon alloys containing from 14 to 33.4 weight per cent silicon has been studied by a number of investigators, whose results have been reviewed in a monograph published by the Engineering Foundation<sup>1</sup>. In these previous researches, the solubility of silicon in iron was determined by thermal, microscopic or magnetic methods and the compound  $\text{Fe}_3\text{Si}_2$  was reported to be stable at temperatures from 0 to approximately  $1030^\circ\text{C}$ . This paper describes the results of an X-ray investigation of the solubility of silicon in iron and gives data which prove that the  $\text{Fe}_3\text{Si}_2$  phase is unstable below  $825^\circ\text{C}$ .

In order to obtain the present results on the solubility of silicon in iron, the authors have utilized the lattice constants of the alpha-phase iron-silicon alloys given in a previous publication<sup>2</sup>, and also some additional data which will subsequently be described.

## MATERIALS AND METHODS

The alloys used in this investigation are listed in Table 1. They were prepared in 30 or 50-gram ingots by melting specially purified silicon and electrolytic or carbonyl iron in alundum crucibles under a pressure of less than 1 mm. of mercury. The purity of the silicon, electrolytic and carbonyl irons has been given by the authors in previous publications<sup>2,5</sup>.

The ingots were homogenized in vacuo at approximately  $1000^\circ\text{C}$ . for at least 96 hr. and then slowly cooled. The homogenized specimens were ground to powder in a hardened steel mortar. This powder was passed through a 150 or 200-mesh screen and sealed in evacuated quartz, Jena or Pyrex glass tubes and heat-treated as noted in the various tables. Specimens 23A, 24B, 33 and 35 and the specimens heated for one month at  $700^\circ\text{C}$ . were quenched by quickly removing the tubes from a horizontal tubular furnace and dropping them into water. The other specimens were quenched by means of a drop-quenching device, which has been described previously<sup>3</sup>.

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<sup>1</sup> References are at the end of the paper.

Temperatures up to and including 1110° C. were measured by means of a platinum-platinum-rhodium thermocouple that had been checked against a Bureau of Standards calibrated thermocouple. The maximum error in the temperatures below 1000° C. may be considered to be  $\pm 5^\circ$  C. The temperature of 1150° C. was measured by means of an optical pyrometer.

The alloys were analyzed for their iron contents by the silver reductor method, using standardized ceric sulfate solutions for titration with ferrous phenanthroline as indicator<sup>8</sup>. Duplicate determinations were made in every case. Silicon was obtained by difference.

TABLE 1.—*Composition of Alloys*

Alloy No.	24	78	23	80	33	34	35	47
Wt. per cent of silicon	16.84	18.69	20.38	22.12	24.75	25.06	29.96	33.40

Focusing cameras designed by Phragmén were used for determining the lattice constants. The total number of X-ray reflections from the 211, 220 and 310 planes, which were measured and used in determining the lattice constants of the respective alloys, are given in Table 4. The error in determining the lattice constants of all the alloys quenched from 600° to 1110° C. may be set at  $\pm 0.0005\text{\AA}$ . In alloy No. 35, quenched from 1150° C., only one alpha-phase reflection could be measured because of the poor quality of the lines resulting from quenching the alloy near its melting point.

Radiation from an iron target was used throughout the investigation. The wave lengths were those assigned by Siegbahn (1931).

### ALLOY PHASES CONSIDERED

In an investigation of the iron-silicon system, Phragmén<sup>4</sup> found two phases, each of which was in equilibrium with the body-centered cubic alpha-iron phase over a certain temperature range. At high temperatures, the second phase was the compound FeSi, which has a cubic structure with four molecules in the unit cell. At about 1030° C. (see references 6, 7 or 1) the following reaction occurs:



The Fe<sub>3</sub>Si<sub>2</sub> structure is very complicated and has not yet been described. It has been supposed that this phase is stable between 1030° C. and room temperature. Thus in this temperature range for alloys adjoining the alpha phase and containing up to 33.4 wt. per cent silicon, there would be two two-phase regions separated by the very narrow single-phase region (Fe<sub>3</sub>Si<sub>2</sub>), the order being: (1) alpha, (2) alpha + Fe<sub>3</sub>Si<sub>2</sub>, (3) Fe<sub>3</sub>Si<sub>2</sub>, (4) Fe<sub>3</sub>Si<sub>2</sub> + FeSi, (5) FeSi.

*Decomposition of Fe<sub>3</sub>Si<sub>2</sub> Phase.*—During the investigation of the alpha-phase solubility limit, it was observed that the FeSi phase was present

in the alloys containing between 17 and 25 wt. per cent silicon when heated to temperature below 850° C. for reasonably long periods of time. The same thing had been noted by other investigators<sup>4,5</sup> and was reasonably interpreted as being due to the slowness of reaction A between the alpha and FeSi phases. However, an X-ray diffraction pattern from the FeSi phase was observed in alloy No. 24, which contained 16.8 wt. per cent silicon. According to Fig. 1 and other iron-silicon<sup>1</sup> phase diagrams, the FeSi phase does not occur in such an alloy at any temperature. Consequently, the occurrence of the FeSi phase in this alloy led the present investigators to suspect that the Fe<sub>3</sub>Si<sub>2</sub> phase became unstable at some temperature below 850° C. and was decomposed into alpha + FeSi, which is the reverse of reaction A.

TABLE 2.—*Phases Present in Alloys at Various Temperatures*

Alloy No.	Weight Per Cent Silicon	Annealing Time	Quenching Temperature, Deg. C.	Phases Present from X-ray Films
24-4	16.84	1 month	700	alpha + FeSi
78-4	18.69	1 month	700	alpha + FeSi
23-4	20.38	1 month	700	alpha + FeSi + (Fe <sub>3</sub> Si <sub>2</sub> very small)
80-4	22.12	1 month	700	alpha + FeSi + (Fe <sub>3</sub> Si <sub>2</sub> small)
34-3	25.06	6 days	700	alpha + FeSi + (Fe <sub>3</sub> Si <sub>2</sub> small)
35-4	29.96	1 month	700	alpha + FeSi + (Fe <sub>3</sub> Si <sub>2</sub> very small)
47-4	33.40	1 month	700	FeSi
24-3	16.84	6 days	850	alpha + Fe <sub>3</sub> Si <sub>2</sub>
78-3	18.69	6 days	850	alpha + Fe <sub>3</sub> Si <sub>2</sub>
23-3	20.38	7 days	852	alpha + Fe <sub>3</sub> Si <sub>2</sub>
80-3	22.12	7 days	852	alpha + Fe <sub>3</sub> Si <sub>2</sub>
34-3	25.06	6 days	857	Fe <sub>3</sub> Si <sub>2</sub> + (FeSi small)
35-3	29.96	7 days	856	Fe <sub>3</sub> Si <sub>2</sub> + FeSi
47-3	33.40	7 days	856	FeSi + (Fe <sub>3</sub> Si <sub>2</sub> trace)
24-3	16.84	7 days	970	alpha
78-2	18.69	1 day	968	alpha + Fe <sub>3</sub> Si <sub>2</sub>
23-3	20.38	7 days	972	alpha + Fe <sub>3</sub> Si <sub>2</sub>
80-2	22.12	1 day	958	alpha + Fe <sub>3</sub> Si <sub>2</sub>
35-3	29.96	7 days	965	FeSi + Fe <sub>3</sub> Si <sub>2</sub>
47-3	33.40	7 days	965	FeSi + (Fe <sub>3</sub> Si <sub>2</sub> trace)
34-G	25.06	4½ hr.	988	Fe <sub>3</sub> Si <sub>2</sub> + (FeSi small)
33-G	24.75	2 hr.	1020	Fe <sub>3</sub> Si <sub>2</sub> + (FeSi small)
35-J	29.96	2½ hr.	1150	alpha + FeSi

In order to confirm this instability of the Fe<sub>3</sub>Si<sub>2</sub> phase at temperatures below 850° C., a series of alloys was heat-treated and the phases present determined by X-ray diffraction patterns, as indicated in Table 2. Alloy

No. 24<sup>r</sup> (16.8 wt. per cent silicon) contains  $\alpha$  + FeSi at 700° C., while it contains  $\alpha$  +  $\text{Fe}_3\text{Si}_2$  at 850° C. and only  $\alpha$  at 970° C. Alloy No. 35 (30 wt. per cent silicon) contains  $\alpha$  + FeSi in addition to a small quantity of  $\text{Fe}_3\text{Si}_2$  at 700° C., while it contains FeSi +  $\text{Fe}_3\text{Si}_2$  at 856° C. and 965° C. The presence of the small quantity of  $\text{Fe}_3\text{Si}_2$  in a number of the alloys after heating to 700° C. for one month indicated that the  $\text{Fe}_3\text{Si}_2$  phase decomposes very slowly into  $\alpha$  + FeSi. The slow rate of the reaction is probably the reason it has not been observed in the thermal analyses of previous investigators.

*Stability Range of  $\text{Fe}_3\text{Si}_2$  Phase.*—As previously stated, the  $\text{Fe}_3\text{Si}_2$  phase is formed on cooling by reaction of  $\alpha$  and FeSi phases (reaction A). The reaction temperature has been placed at 1030° C. by Haughton and Becker<sup>6</sup> and this represents the upper temperature limit for the stable existence of the  $\text{Fe}_3\text{Si}_2$  phase.

It has been shown above that the  $\text{Fe}_3\text{Si}_2$  phase decomposes below 850° C. (approximately) according to the same reaction equation (reaction A). An attempt was made to establish this lower decomposition temperature within narrow limits. In these experiments an alloy containing 25.06 wt. per cent silicon, which corresponds almost exactly to the theoretical composition of  $\text{Fe}_3\text{Si}_2$  (25.09 wt. per cent), was heat-treated as noted in Table 3. The samples marked "R" were heated to 857° C. for six days in order to convert them to FeSi +  $\text{Fe}_3\text{Si}_2$  phases. The samples marked "Q" were heated for six days at 700° C. to convert them

TABLE 3.—*Determination of Lower Decomposition Temperature of the  $\text{Fe}_3\text{Si}_2$  Phase<sup>a</sup>*

Sample No.	Quenching Temperature, Deg. C.	Observed Diffraction Patterns of Phases
1R <sup>b</sup>	857	FeSi + $\text{Fe}_3\text{Si}_2$
2R	841	FeSi + $\text{Fe}_3\text{Si}_2$
3R	817	FeSi + $\text{Fe}_3\text{Si}_2$ + ( $\alpha$ trace)
4R <sup>c</sup>	790	FeSi + $\text{Fe}_3\text{Si}_2$ + ( $\alpha$ weak)
5R	770	$\alpha$ + FeSi + $\text{Fe}_3\text{Si}_2$
1Q	841	$\alpha$ + FeSi + $\text{Fe}_3\text{Si}_2$ (strong)
2Q	817	$\alpha$ + FeSi + ( $\text{Fe}_3\text{Si}_2$ weaker than No. 5Q)
3Q <sup>d</sup>	790	$\alpha$ + FeSi + ( $\text{Fe}_3\text{Si}_2$ weak)
4Q	770	$\alpha$ + FeSi + ( $\text{Fe}_3\text{Si}_2$ weaker than No. 1Q)
5Q <sup>b</sup>	700	$\alpha$ + FeSi + ( $\text{Fe}_3\text{Si}_2$ weaker than No. 1Q)

<sup>a</sup> Alloy 34 containing 25.06 wt. per cent silicon was used to obtain these data.

<sup>b</sup> Nos. 1R and 5Q were the original samples of each group, the others were subsequently heat-treated (6 days) portions of the original samples.

<sup>c</sup> Heated for 6 days at 857°, then 6 days at 841°, finally cold-worked and heated 11 days at 790° C.

<sup>d</sup> Heated for 11 days at 790° C.

to  $\alpha$  + FeSi phases, although this latter conversion was not quite complete. Portions of the samples treated at 857° and 700° C. were then heated for another six days at the temperatures indicated. (The specimens 4R and 3Q were treated somewhat differently; see Table 3.) It is evident from Table 3 that the decomposition temperature lies between 817° and 841° C. and is probably close to 825° C.

It may be noted that the occurrence of the X-ray diffraction pattern from the FeSi phase, but not from the  $\alpha$  phase, in alloys 33 and 34 (24.75 and 25.06 wt. per cent silicon respectively) at 841° C., 857° C., 988° C. and 1020° C., indicates that the  $\text{Fe}_3\text{Si}_2$  phase contains somewhat more iron than is required by the theoretical composition of the compound (74.91 wt. per cent Fe). The exact amount of this excess has not been determined.

It has also been observed that the decomposition of the  $\text{Fe}_3\text{Si}_2$  phase by heating above 1030° C. is by no means rapid. In several cases two or three hours at temperatures of 1050° or 1060° C. had little more than started the decomposition.

#### DETERMINATION OF SOLUBILITY OF SILICON IN IRON

The solubility of silicon in iron was determined by comparing the lattice constants of the  $\alpha$  phase in the two-phase alloys with the lattice constants of the single-phase  $\alpha$  alloys. According to this method, the lattice constants of the  $\alpha$  phase in the quenched two-phase alloys are equal to the lattice constants of the  $\alpha$  phase at the solubility limit for the respective temperatures from which the two-phase alloys have been quenched. The method implies, of course, that the two phases in the quenched specimens were in equilibrium at the quenching temperature and that no change occurred during quenching.

In a previous publication<sup>2</sup> the authors have shown that the plot of lattice constants vs. atomic per cent silicon is a straight line for the iron-silicon alloys containing from 9 to 25.8 atomic per cent (4.7 to 14.8 wt. per cent) silicon. This line was extrapolated to approximately 34 atomic per cent (20.5 wt. per cent) silicon in order to obtain the lattice constants of the  $\alpha$  phase at the higher temperatures where the solubility is greater than the above limit. The lattice constants of the  $\alpha$  phase in the two-phase alloys were determined as previously described.\*

The data on the solubility of silicon in iron are given in Table 4 and plotted in Fig. 1. This curve shows that the solubility of silicon in iron increases from 15.2 wt. per cent silicon at 600° C. to 20.4 wt. per cent

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\* The original work was checked over the range important for this investigation by new samples of several alloys made in the earlier investigation. The agreement was well within the experimental error of the measurements. The lattice constant of alloy No. 24 quenched from 970° C. agreed fairly well with this curve, although the diffraction lines were too spotty for accurate results.



silicon at 1030° C. For the temperatures from 1030° to 1150° C. the solubility limit is approximately constant at 20.4 wt. per cent silicon. The maximum deviation of the points from the curve between 600° and 990° C. is approximately 0.2 wt. per cent silicon. In the temperature range above 990° C. the solubility limit has been less definitely established than in the lower temperature range because the diffraction lines on the films are not sharply defined and, consequently, there is a lower degree of precision in the determination of the lattice constants. The solubility curve has been drawn with a discontinuity at 825° C. (16.6 wt. per cent

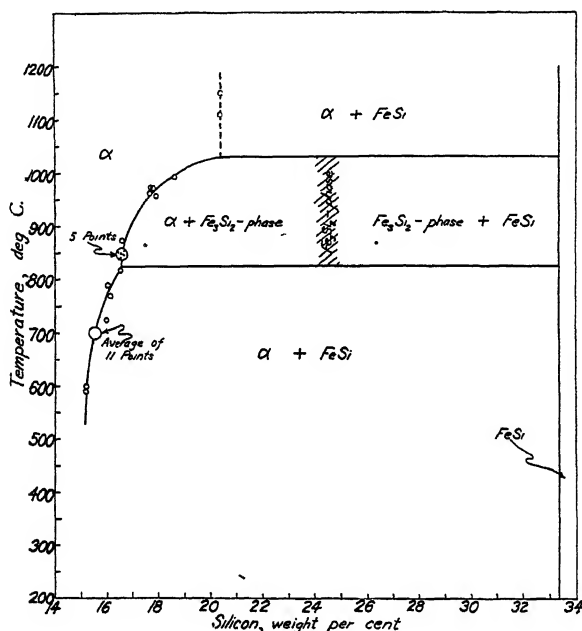


FIG. 1.—CONSTITUTION OF IRON-SILICON ALLOYS CONTAINING FROM 14 TO 33.4 PER CENT SILICON.

silicon) to correspond to the transformation that occurs at or close to that temperature.\* A plot of the reciprocal absolute temperature against the logarithm of atomic per cent silicon gave sharply curved lines indicating that these solutions are far from ideal.

\* The large number of points concentrated at the temperatures 700°, 850° and 960° C. resulted from the fact that the experiments reported in Tables 2 and 3 frequently gave films that were suitable for solubility determinations. It was thought to be of some general interest to demonstrate how closely results of X-ray determinations of solubility could be checked on alloys of different compositions and annealed for various lengths of time. Table 4 also shows that the presence of very small amounts of a third phase, indicating failure to reach final equilibrium, did not affect the solubility determination beyond the other experimental errors in this particular investigation.

TABLE 4.—*Solubility of Silicon in Alpha Iron*

Alloy No.	Quenching Temperature, Deg. C.	Heat Time, Hr.	Number of Diffraction Lines Measured	$a_0$ for $\alpha$ Phase	Solubility of Silicon	
					Atomic Per Cent	Weight Per Cent
78	590	930	7	2.8185	26.33	15.20 <sup>a</sup>
23-A	600	83	6	2.8183	26.40	15.25 <sup>a</sup>
24-B-3	697	258	6	2.8178	26.65	15.45
24-3	700	168	7	2.8175	26.80	15.55
24-4	700	820	7	2.8181	26.54	15.36
78-3	700	168	7	2.8177	26.68	15.46
78-4	700	820	7	2.8172	26.95	15.65
23-3	700	168	6	2.8176	26.77	15.52 <sup>a</sup>
23-4	700	820	7	2.8174	26.83	15.56 <sup>a</sup>
80-3	700	168	7	2.8177	26.68	15.46 <sup>a</sup>
80-4	700	820	7	2.8176	26.77	15.52 <sup>a</sup>
35-3	700	168	5	2.8179	26.62	15.42 <sup>a</sup>
35-4	700	820	4	2.8172	26.95	15.65 <sup>a</sup>
24-B	724	85	7	2.8161	27.45	16.00 <sup>a</sup>
34-3-1	770	144 <sup>b</sup>	5	2.8156	27.70	16.16 <sup>a</sup>
34-3	790	268 <sup>b</sup>	7	2.8159	27.56	16.06 <sup>a</sup>
34-3-3	817	144 <sup>b</sup>	4	2.8144	28.30	16.57 <sup>a</sup>
24-6	842	70	6	2.8145	28.25	16.55
24-D	846	65	6	2.8141	28.45	16.68
24-3	850	149	6	2.8144	28.30	16.57
23-3	852	168	6	2.8140	28.48	16.70
80-3	852	168	3	2.8147	28.15	16.48
23-D	874	22	6	2.8142	28.40	16.62
80-2	958	24	4	2.8101	30.30	17.95
23-E	962	11	4	2.8109	29.97	17.70
80-1	972	1.3	3	2.8102	30.10	17.85
23-1	974	1.3	4	2.8108	30.00	17.75
23-F	992	15	4	2.8081	31.30	18.63
33	1110	2.5	4	2.8028	33.80	20.41
35	1150	2.5	1	2.803	33.8	20.4

<sup>a</sup> Not quite at equilibrium; a small quantity of third phase, usually a barely observable trace, still present.

<sup>b</sup> Prior treatment at 700° C. for 144 hours.

## DISCUSSION OF RESULTS

The results of this investigation are shown in the constitutional diagram of Fig. 1. The transformation at 1030° C. was observed by Haughton and Becker. Murakami, who investigated less pure alloys than Haughton and Becker, placed the temperature of the same transformation at 1020° C. The transformation at 825° C. was observed in the present investigation. Above the 1030° C. transformation alpha and FeSi coexist. Below the 1030° C. transformation and above the 825° C. transformation there are two two-phase regions; namely, alpha + Fe<sub>3</sub>Si<sub>2</sub>, and FeSi + Fe<sub>3</sub>Si<sub>2</sub>. For temperatures below 825° C., alpha and FeSi coexist between the alpha solubility limit and the FeSi phase.

It should be noted that the films from alloy No. 47 (33.40 wt. per cent silicon) quenched from 700°, 856° and 965° C. and alloy No. 35 quenched from 1150° C. show no difference in the FeSi patterns. This means that within these temperature limits there was no detectable change in the FeSi structure.\*

The solubility of silicon in iron determined in the present investigation roughly parallels the limits reported by Haughton and Becker<sup>6</sup>, and by Murakami<sup>7</sup>. The limits given by Haughton and Becker are approximately one weight per cent silicon lower at temperatures between 600° C. and 1030° C., while the limits given by Murakami are approximately one per cent higher at the temperatures between 600° and 950° C. than those observed in the present investigation. The differences between these several sets of determinations are very probably due to the slowness of the transformations in the solid state.

## SUMMARY

A portion of the iron-silicon phase diagram in the range 14 to 33.4 wt. per cent silicon has been investigated by X-ray methods.

It has been shown that the Fe<sub>3</sub>Si<sub>2</sub> phase, which forms by reaction between alpha and FeSi at 1030° C. (Haughton and Becker), also decomposes at or close to 825° C. into alpha and FeSi. This Fe<sub>3</sub>Si<sub>2</sub> phase is thus stable only between 825° and 1030° C.

The solubility limits of silicon in alpha iron between 600° and 1150° C. have been determined. The results differ from those of previous investigators.

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\* The presence of traces of Fe<sub>3</sub>Si<sub>2</sub> lines on the films of this alloy (No. 47, quenched from 856° and 965° C.), which has a composition very close to the theoretical composition of FeSi (33.44 wt. per cent silicon), gives rise to the suspicion that perhaps this phase also does not occur at precisely the theoretical composition. This point has not been investigated in detail. It may be observed that since Phragmén<sup>4</sup> has found the same type of phenomenon for FeSi<sub>2</sub>, this would make all three of the intermediary phases in the iron-silicon system "abnormal" with respect to stoichiometrical ideality.

## ACKNOWLEDGMENTS

The writers take this opportunity to acknowledge their indebtedness to Mr. Frank Foote, Research Assistant in Metallurgy, whose timely assistance at various stages of the investigation considerably expedited the work; Mr. Bodie Pryor, graduate student in chemical engineering, who made a number of the chemical analyses, and otherwise assisted in the experimental work; The National Youth Administration, which furnished the services of Mr. Pryor as well as several other assistants who have helped at various stages of the investigation; The Electro Metallurgical Company of New York, for the very pure silicon used in this work.

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## Studies upon the Widmanstätten Structure, VIII—The Gamma-alpha Transformation in Iron-nickel Alloys

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(New York Meeting, February, 1937)

THE gamma-alpha transformation in iron and iron-rich alloys is of such practical and theoretical importance that many papers have been published upon the subject relating to critical temperatures, transformation rates and accompanying property changes. Although crystallographic studies are of less immediate practical usefulness, the opportunities which these offer to furnish data on the basic atomic movements which characterize the transformation are not to be neglected<sup>1</sup>. The early work on the crystallography of this transformation has been reviewed in the fourth paper of this series<sup>2</sup>; since then several important papers have appeared. Our present knowledge may be briefly summarized as follows.

Kurdjumow and Sachs, working with a 1.4 per cent carbon steel<sup>3</sup>, established the orientation relationships subsisting between the face-centered gamma and the metastable tetragonal lattices in freshly quenched martensite, and between the face-centered gamma and the body-centered alpha lattices in tempered martensite. The orientation relationship observed in the latter case may be stated in terms of planes and directions observed to lie parallel in the two lattices:

$$\begin{array}{l} \{111\}_{\gamma} // \{110\}_{\alpha} \\ [110]_{\gamma} // [111]_{\alpha} \end{array}$$

(This notation is used throughout as the most descriptive means of expressing the fact that any (111) plane of the gamma phase may be parallel to any (110) plane of the alpha phase, and that a [110] direction in a particular (111)<sub>γ</sub> plane is parallel to a [111] direction in the corresponding (110)<sub>α</sub> plane.) From these relationships the atomic movements that transform the gamma lattice into the alpha may be inferred. In the present experiment these may be considered as consisting primarily in a shear of the atoms parallel to the {111}<sub>γ</sub> planes in [110]<sub>γ</sub> directions

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<sup>1</sup> References are at the end of the paper.

and secondarily in a shear normal to this direction, together with an adjustment in interatomic distances; the operation of such shearing movements was postulated in the first paper of this series.

It was then shown<sup>2</sup> that the orientation of proeutectoid ferrite in hypoeutectoid iron-carbon alloys could be represented by a set of relationships similar to those given above, though the precision of the work was not high; it was later shown that the orientation relationships between the gamma and alpha phases in pure iron could be represented by the same set of specifications, though the precision of this work was even lower<sup>4</sup>. The early X-ray work of Young<sup>5</sup> on the orientation of the kamacite (alpha) phase with respect to the taenite (gamma) phase in meteorites, and the later goniometric work of Bøggild<sup>6</sup> on the same subject disclosed orientation relationships which could be represented by the same specifications though not with great precision. The orientation relationships between the alpha and beta phases in the copper-zinc system, and in other structurally analogous systems, were found to be similar, owing presumably to the identity in the lattice types.<sup>7</sup> Strangely enough, the orientation relationship between the gamma phase and the alpha in pearlite proved to be quite different, as shown by the relationship<sup>8</sup>

$$\begin{array}{l} \{110\}_{\gamma} // \{211\}_{\alpha} \\ [211]_{\gamma} // [110]_{\alpha} \end{array}$$

Similarly the orientations resulting from the eutectoid decomposition of the face-centered cubic beta phase in the copper-aluminum system were found not to be the same as those resulting from proeutectoid precipitation of the face-centered cubic alpha phase<sup>9</sup>.

Thus, apart from eutectoid decompositions, it seemed likely that the orientation relationships between the face-centered cubic and body-centered cubic phases, and thus the transformation mechanism, are determined only by the lattice types involved, and that these relationships should obtain generally in alloys of iron, provided that solid solution formation should not so far alter the relative interatomic distances in the two phases as to radically alter the geometrical relationships of the two lattices. Surprisingly, however, Nishiyama<sup>10</sup> found a somewhat different set of relationships in an iron-nickel alloy with 30 per cent nickel transformed at liquid air temperatures, which may be stated as follows:

$$\begin{array}{l} \{111\}_{\gamma} // \{110\}_{\alpha} \\ [211]_{\gamma} // [110]_{\alpha} \end{array}$$

The atomic movements by which these orientation relationships may be generated can be resolved into a shear of the atoms parallel to the  $\{111\}_{\gamma}$  plane in the  $[211]_{\gamma}$  direction. Recently Wassermann<sup>11</sup> has confirmed the

work of Kurdjumow and Sachs on martensite and that of Nishiyama on iron-nickel alloys.

The alterations in interatomic distance may be suspected as the cause for a change in mechanism with increasing nickel content; in this case the type of mechanism should change at some intermediate nickel content, but since the parameters of both phases are changed only very slightly ( $a_0\gamma$  is increased only 0.3 per cent by 30 per cent nickel) and in the same direction, the difference is insignificant and probably quite unimportant in determining the type of transformation mechanism. Furthermore, the initiation of ferromagnetism in the 30 per cent nickel alloy on cooling before the beginning of transformation might be presumed so far to alter the elastic properties as to initiate a different mechanism. Dehlinger<sup>12</sup> as well as Wassermann<sup>11</sup> has proposed that the substitutional solid solution of nickel in gamma iron may possess shearing properties different from those for the interstitial solid solution of carbon in gamma iron, as suggested by the occurrence of the transitional tetragonal lattice in the latter case and the absence of a transitional lattice in the former case. It is apparent that our understanding of transformation mechanisms will be enhanced if the fundamental cause for the change in mechanism is understood, or at least if the various conditions under which it appears are determined.

The X-ray work of Young, which preceded that of Kurdjumow and Sachs and that of Nishiyama, was of a high order of accuracy with an estimated error of  $\pm 1^\circ$  in orientation; the orientation determined by Young falls within  $3^\circ$  of the orientation showed by Nishiyama and within  $2^\circ$  of that showed by Kurdjumow and Sachs, thus favoring the Kurdjumow and Sachs relationship, though not conclusively. The data of Bøggild are likewise inconclusive—though favoring the Kurdjumow and Sachs relationship.

In order to furnish more conclusive evidence on the orientation relationships obtaining in meteorites and in artificial iron-nickel alloys of various compositions subjected to several types of heat-treatment, a series of experiments was performed which will be reported below.

#### ORIENTATION OF THE ALPHA PHASE IN METEORITES

A Cañon Diablo meteorite with well developed and straight kamacite lamellae, reported to contain about 7 per cent nickel<sup>5</sup>, was selected for study.\* Since the difference in orientation between the positions of the  $\{110\}$  poles in the Kurdjumow and Sachs relationship and the Nishiyama relationship is approximately only  $5^\circ$  (see Fig. 2), it will be evident that a distinction between the two relationships is possible only when the degree of crystal perfection is high. In order to obtain evidence on this

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\* This structure is quite similar to that shown in Fig. 1, ref. 1.

point, the directions taken by a set of parallel kamacite lamellae on the surface of polish—the “trace directions”—were measured in an area 10 in. square. When referred to an arbitrary reference line, the trace directions of a single set of 23 parallel lamellae showed a scatter of  $3.6^\circ$ . It is obvious that the angles of these trace directions could not be used to establish the orientation of the original taenite with high precision.\* Furthermore, a precision back-reflection Laue determination of the orientation of the lattice in 14 kamacite lamellae in an area 2 by 6 in. showed no precise grouping of the  $\{110\}\alpha$  poles. The diffraction spots

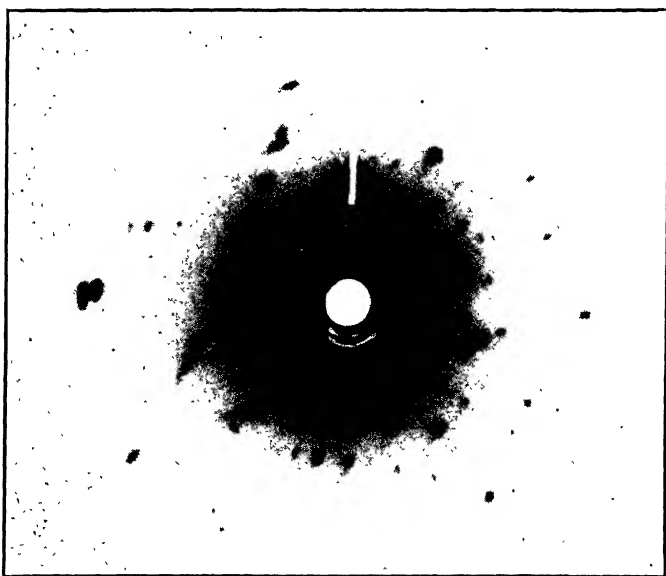


FIG. 1.—BACK-REFLECTION LAUE PHOTOGRAPH OF A KAMACITE PLATE IN A CAÑON DIABLO METEORITE. MOLYBDENUM TARGET. SPECIMEN TO FILM DISTANCE OF 3 CENTIMETERS.

on the back-reflection Laue photographs, however, showed the  $\alpha$ -lattice within each of the lamellae to be of a high degree of perfection (Fig. 1).

Despite the deviations from ideal orientations over large areas, it seemed possible that within a small area of the sample a precision determination of the relative positions of the  $\{110\}\alpha$  poles would afford a plot of poles showing distinct groupings which would allow a choice between the two relationships.

Accordingly, an area  $1\frac{1}{4}$  in. square was selected for study, and the orientation of 18 kamacite lamellae determined by the Laue back-reflection method. The  $\{110\}\alpha$  poles for each of these lamellae were plotted on a single stereographic projection, together with the approximate positions of the  $\{111\}\gamma$  poles determined by the trace directions of the

\* The method is given in reference 1.



kamacite lamellae as indicated above. All of these data were then rotated into a standard unit stereographic triangle. The resultant projection is shown in Fig. 2. It is evident that the  $\{110\}\alpha$  poles are arranged in three distinct groups about the  $(111)\gamma$  pole, though the determination of the  $\{111\}\gamma$  poles is only approximate. Fig. 2 shows also the predicted positions of the  $\{110\}\alpha$  poles for the relationship of Kurdjumow and Sachs and that of Nishiyama, respectively. The Nishiyama relationship requires only two  $\{110\}\alpha$  poles in the neighborhood of the  $(111)\gamma$  pole, whereas the Kurdjumow and Sachs relationship requires three; we may therefore conclude that the orientations of the  $\alpha$  phase in this sample are more nearly in accordance with the relationship of Kurdjumow and Sachs than with that of Nishiyama.

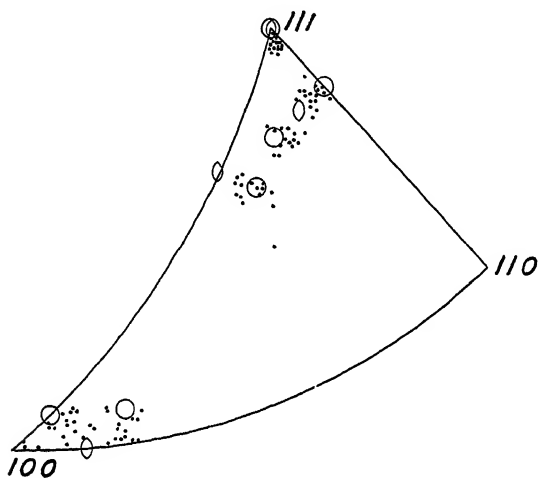


FIG. 2.—UNIT STEREOGRAPHIC TRIANGLE.

Circle indicates the  $\{110\}\alpha$  poles predicted by Kurdjumow and Sachs.

Ellipse indicates the  $\{110\}\alpha$  poles predicted by Nishiyama.

Dots indicate the  $\{110\}\alpha$  poles determined experimentally for 18 kamacite plates.

Gamma poles as designated.

The scatter in orientations shows that the perfection of structure is not high. For this reason, Young's results on only a few random lamellae are of no use in deciding between the two ideal relationships in question.

#### ORIENTATION OF ALPHA PHASE IN IRON-NICKEL ALLOYS

The work of Nishiyama was repeated on an iron-nickel alloy containing 31.36 per cent Ni, 0.70 per cent Mn, 0.03 per cent Si, prepared from electrolytic iron and nickel by induction melting in a magnesia-lined graphite crucible.\* The alloy was annealed in hydrogen at approximately 1400° C. for two weeks in order to grow large grains and inci-

\* This alloy was supplied to us through the courtesy of Mr. Howard Scott of the Westinghouse Research Laboratories, Pittsburgh, Pa.

dentally to purify it by removing carbon, nitrogen and oxygen. The resultant alloy contained grains 5 mm. in diameter on a polished surface, which is large enough for the X-ray pole-figure work. Back-reflection Laue photograms showed the grains to be very perfect in structure (Fig. 3).

As prepared, the samples were composed only of the  $\gamma$ -phase. By trial it was found that treatment in carbon dioxide-acetone mixtures at  $-70^{\circ}\text{C}$ . and in liquid nitrogen at  $-195^{\circ}\text{C}$ ., gave partial transformation to the  $\alpha$ -phase, that the particles of the  $\alpha$ -phase were sufficiently coarse



FIG. 3.—BACK-REFLECTION LAUE PHOTOGRAM OF A GRAIN OF 31 PER CENT NI IRON-NICKEL ALLOY. MOLYBDENUM TARGET. SPECIMEN TO FILM DISTANCE 3 CENTIMETERS.

and the lattice of the  $\alpha$ -phase sufficiently perfect to give individual diffraction spots on Davey-Wilson films made on a Weissenberg camera. In each case appreciable quantities of the  $\gamma$ -phase remained, thus permitting a simultaneous determination of the orientations of the  $\gamma$  and  $\alpha$  phases. The reflections obtained from samples transformed at  $-70^{\circ}\text{C}$ . were fewer in number and more sharply defined.

*Thirty-one Per Cent Nickel Alloy, Transformed at  $-70^{\circ}\text{C}$ .*—Photograms of 13 grains transformed at  $-70^{\circ}$ , containing both the  $\alpha$  and  $\gamma$  phases, were taken partly with  $\text{FeK}\alpha$  radiation and partly with  $\text{CrK}\alpha$  radiation. The data showing the relation of  $\{110\}$   $\alpha$ -poles to the  $\gamma$ -orientations were plotted and rotated into a unit stereographic triangle. These show a rather considerable degree of scatter, doubtless owing partly to the changes of volume accompanying the transformation. To eliminate

this, samples were cut in plates 1 mm. thick and rods 1 mm. in diameter, and etched to 50 per cent loss in weight. The samples were immersed

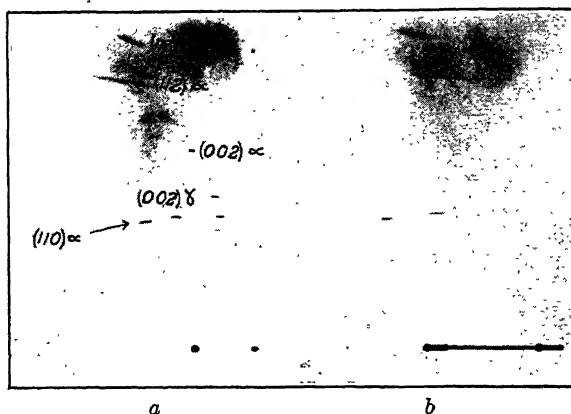


FIG. 4.—DAVEY-WILSON FILMS OF A PARTIALLY TRANSFORMED GRAIN OF THE 31 PER CENT NI IRON-NICKEL ALLOY, COPPER RADIATION.  
a, stationary film; b, oscillating film.

in carbon dioxide-acetone at  $-70^{\circ}$  only momentarily in order that only a small amount of the  $\alpha$ -phase should form and thus that the distortion

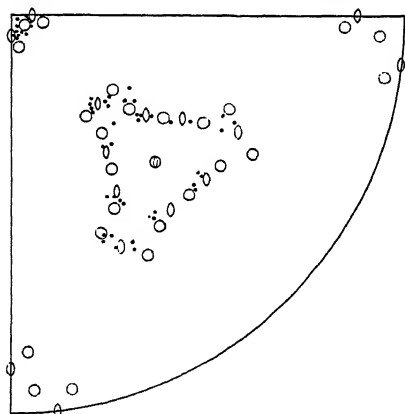


FIG. 5.—STEREOGRAPHIC PROJECTION OF ALPHA ORIENTATIONS IN 31 PER CENT NI IRON-NICKEL ALLOY SAMPLES TRANSFORMED AT  $-70^{\circ}$  C.

Circle indicates the  $\{110\}\alpha$  poles predicted by Kurdjumow and Sachs.

Ellipse indicates the  $\{110\}\alpha$  poles predicted by Nishiyama.

Dots indicate the  $\{110\}\alpha$  poles determined experimentally.

should be kept at a minimum. A typical set of Davey-Wilson films is shown in Fig. 4. The orientations of the components in 13 different grains were determined as before and the results plotted stereographically, as shown in Fig. 5.\* The degree of scatter is still marked, and, as may be seen in Fig. 5, a choice between the Kurdjumow and Sachs and the Nishiyama relationships is not possible. In view of the perfection of the  $\gamma$ -crystal and the sharp reflections obtained from the  $\alpha$ -grains, it is unlikely that all of this scatter can be due to distortion arising from the transformation.

It is to be remembered that the Widmanstätten figure in the meteorite studied was probably formed

at a relatively high temperature during extremely slow cooling,

\* In this and subsequent experiments the  $\{100\}\alpha$  and  $\{110\}\alpha$  poles were both plotted; only the  $\{110\}$  data are reported for the sake of brevity.

and that the sample studied by Nishiyama was transformed at liquid-air temperature. Thus, if we assume that the Kurdjumow and Sachs relationship obtains when the transformation proceeds at a high temperature, as shown by the present work on meteorites, and that the Nishiyama relationship occurs when the transformation proceeds at low temperatures, as shown by Nishiyama's work, we may accept the scatter shown in Fig. 5 as caused probably by a combination of the two mechanisms obtaining on transformation at an intermediate temperature. Remembering that the relationships of Kurdjumow and Sachs and of Nishiyama can both be described as shearing processes, it is not difficult to imagine that at these temperatures both types of shear occur in a way analogous to double slip on plastic deformation, resulting in orientations which are intermediate between those predicted by the two ideal mechanisms. It will be noted that the Kurdjumow and Sachs' relationships in martensite were created on transformation at a relatively high temperature; i.e., on quenching in water. If, then, it is demonstrated that in a *single composition* of these alloys the Kurdjumow and Sachs relationship obtains when the transformation is effected at a high temperature, and the Nishiyama at a low temperature, a new and fundamental fact will be added to our knowledge of transformations.

*Thirty-one Per Cent Nickel Alloy Transformed at  $-195^{\circ}\text{C}$ .*—Thin samples, similar to those described above, were transformed in liquid nitrogen at  $-195^{\circ}$  and photograms prepared of four different  $\gamma$ -grains. The stereographic plot of the results (Fig. 6) shows that the Nishiyama relationship obtains.

*Thirty-one Per Cent Nickel Alloy Transformed at  $240^{\circ}\text{C}$ .*—Several grains in a 31 per cent Ni sample were transformed by annealing at  $240^{\circ}\text{C}$ . for six days,\* producing a platelike microstructure, closely simulating the Widmanstätten figure in meteorites (Fig. 7). This microstructure is quite different in appearance from the martensite-like structure produced at low temperatures (Fig. 8). The X-ray orientation data (Fig. 9) are in close agreement with the Kurdjumow and Sachs relationship. Thus at  $240^{\circ}$  this alloy transforms in accordance with the Kurdjumow and

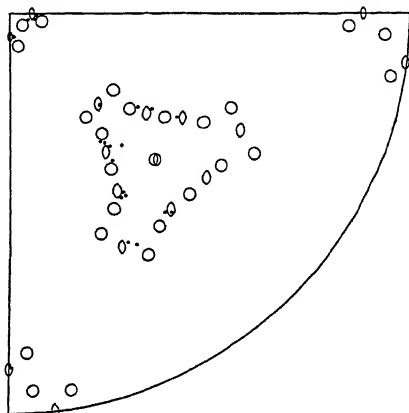


FIG. 6.—STEREOGRAPHIC PROJECTION OF ALPHA ORIENTATIONS IN 31 PER CENT NI IRON-NICKEL ALLOY SAMPLES TRANSFORMED IN LIQUID NITROGEN.

\* There are two temperature regions where the gamma-alpha transformation occurs rapidly<sup>12</sup>. See also ref. 12.

Sachs relationship, at  $-70^{\circ}$  it transforms with a mixed relationship, including both the Kurdjumow and Sachs and the Nishiyama, and at  $-195^{\circ}$  with a Nishiyama relationship.



FIG. 7.—GRAIN OF 31 PER CENT NI IRON-NICKEL ALLOY TRANSFORMED AT  $240^{\circ}$  C.  
 $\times 140$ . NITAL ETCH.

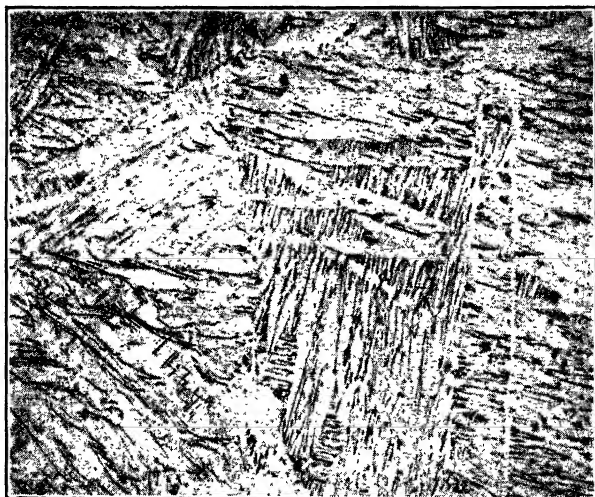


FIG. 8.—GRAIN OF 31 PER CENT NI IRON-NICKEL ALLOY TRANSFORMED AT  $-195^{\circ}$  C.  
 $\times 50$ . NITAL ETCH.

In order to study the effect of composition upon the orientation relationships following transformation at different temperatures, a series of

iron-nickel alloys was prepared with 27, 28, 28.5 and 34 per cent Ni. Pure gamma could be retained by quenching to 0° C. only in alloys containing 28.5 per cent Ni or above—the 27 per cent and 28 per cent alloys partially transformed on quenching; alloys with more than 34 per cent Ni cannot be transformed within reasonable times at any temperature. In preparing these alloys, carbonyl iron and electrolytic nickel were melted in vacuo in high-purity alumina crucibles. The ingots, averaging 30 grams, were hot-forged in air and homogenized in hydrogen at 1100° C. for periods varying from three to seven days. They were finally heated to 1400° C. to permit the growth of large grains and then furnace-cooled.

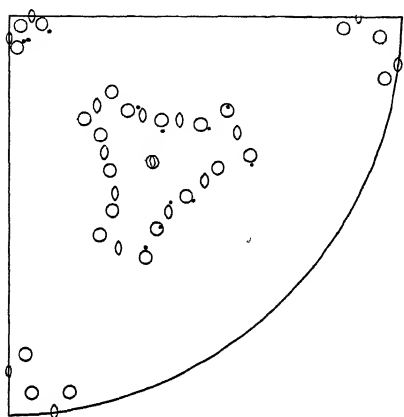


FIG. 9.

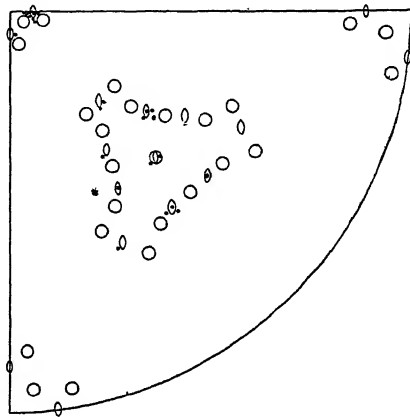


FIG. 10.

FIG. 9.—STEREOGRAPHIC PROJECTION OF ALPHA ORIENTATIONS IN 31 PER CENT NI IRON-NICKEL ALLOY SAMPLE TRANSFORMED AT 240° C.

FIG. 10.—STEREOGRAPHIC PROJECTION OF ALPHA ORIENTATIONS IN 34 PER CENT NI IRON-NICKEL ALLOY SAMPLES TRANSFORMED IN LIQUID NITROGEN.

Circle indicates the  $\{110\}\alpha$  poles predicted by Kurdjumow and Sachs.

Ellipse indicates the  $\{110\}\alpha$  poles predicted by Nishiyama.

Dots indicate the  $\{110\}\alpha$  poles determined experimentally.

The lower nickel samples were quenched from 250° C. into mercury at 0° C.

*Thirty-four Per Cent Nickel Alloy Transformed at -195° C.*—Four different sections of the 34 per cent Ni alloy were transformed by immersion in liquid nitrogen, and a Davey-Wilson photogram made of one large grain on each sample. The data from these films (Fig. 10) show that the orientations are accurately defined by the relation of Nishiyama.

*Twenty-seven Per Cent Nickel Alloy, Furnace-cooled.*—Quenching experiments failed to retain the  $\gamma$ -phase of the 27 per cent Ni samples completely, and for this reason no attempt was made to study the transformation of this alloy in liquid nitrogen. One sample, however, was allowed to cool to room temperature in the furnace, whence developed the exceptionally regular Widmanstätten pattern shown in Fig. 11. The individual lamellae can be distinguished without magnification, and it

is believed to be the best figure that has yet been produced artificially in

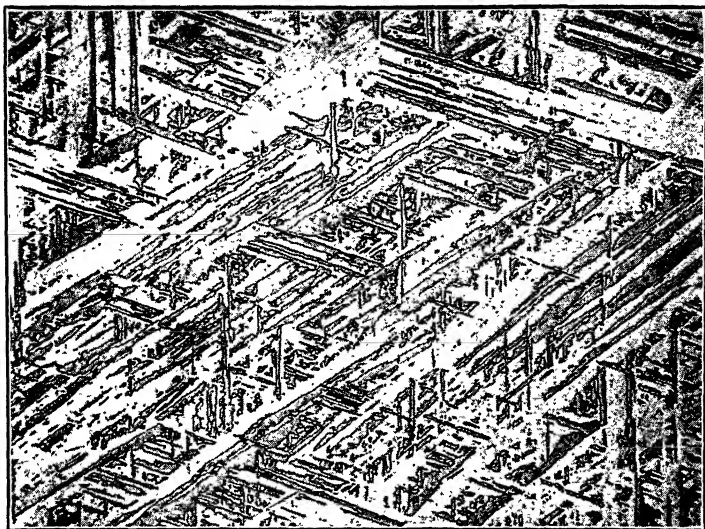


FIG. 11.—WIDMANSTÄTTEN FIGURE IN A SLOWLY COOLED 27 PER CENT NI IRON-NICKEL ALLOY.  $\times 50$ . NITAL ETCH.

alloys of iron and nickel. The gamma orientation of this grain was

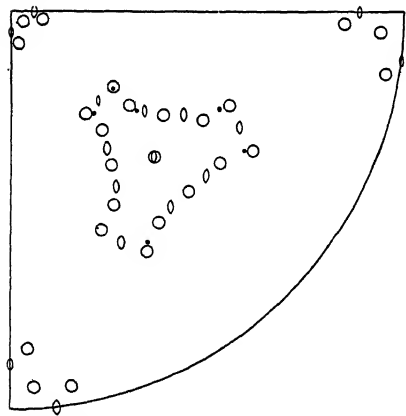


FIG. 12.—STEREOGRAPHIC PROJECTION OF ALPHA ORIENTATIONS IN 27 PER CENT NI IRON-NICKEL ALLOY TRANSFORMED BY SLOW COOLING.

Circle indicates the  $\{110\}\alpha$  poles predicted by Kurdjumow and Sachs.

Ellipse indicates the  $\{110\}\alpha$  poles predicted by Nishiyama.

Dots indicate the  $\{110\}\alpha$  poles determined experimentally.

determined by measuring the trace directions, and the  $\{110\}\alpha$  poles were found by the Davey-Wilson method. The plot of these data (Fig. 12) shows that the alpha orientations can be described by the relation of Kurdjumow and Sachs.

*Twenty-eight Per Cent Nickel Alloys.*—The gamma phase of 28.5 per cent Ni alloys was retained completely by quenching. Samples were subsequently transformed on one hand by heating at  $250^\circ$  for one week in an evacuated Pyrex tube, and on the other hand by momentary immersion in liquid nitrogen. Analysis by the methods already described showed that the high-temperature transformation can be described by the Kurdjumow and Sachs relationship, whereas the low-temperature transformation requires the Nishiyama relationship. These data are in

complete agreement with those shown in Figs. 6 and 9; consequently, no additional figure is shown.

### DISCUSSION OF RESULTS

It has thus been shown that the orientations of the  $\alpha$ -phase kamacite and the  $\gamma$ -phase taenite in a meteorite with 7 per cent Ni exhibiting a Widmanstätten figure may be described by the orientation relationship of Kurdjumow and Sachs, and that iron-nickel alloys of higher nickel contents likewise exhibit this relationship when the  $\alpha$ -phase forms on slow cooling or by reheating above room temperature.\* When, however, these same high-nickel alloys transform at  $-195^{\circ}$  C. the orientation relationships may be described by the mechanism of Nishiyama; at  $-70^{\circ}$ , which may be taken as an intermediate temperature, neither of these two mechanisms operates uniquely. Thus the orientation relationships existing between the  $\alpha$  and  $\gamma$  phases in these alloys, and therefore the transformation mechanism, is one dependent upon the temperature of transformation alone, and not upon alloy composition.

It follows therefore that the Kurdjumow and Sachs relationship, which previously had been observed only in high-carbon martensitic structures, does not depend for its occurrence upon the formation of a transitional tetragonal lattice characterizing the martensitic structure, as has been suggested<sup>11,12</sup>, for despite careful search<sup>14</sup> no transitional lattices have been found in transformed pure iron-nickel alloys. It follows also that alterations in interatomic distance with solid solution formation or in the ferromagnetic properties, or differences in shearing properties between the interstitial  $\gamma$  solid solution in the iron-carbon system and the substitutional  $\gamma$  solid solution in the iron-nickel system—or indeed of any property held a function of composition alone—cannot be effective in determining which of the two mechanisms shall operate.

The occurrence of two modes of transformation in these alloys, one acting relatively vigorously at an elevated temperature and the other relatively vigorously at a low temperature with an intermediate temperature range in which the rate of transformation is very slow, is similar to the occurrence of the pearlite and martensite reactions in steel, as illustrated by the familiar Bain "S-curve"<sup>15</sup>; this has been clearly recognized for some time<sup>13</sup> though the crystallography of the two modes had not been determined. It will be noted, however, that the crystallographic mechanism operating in the pearlite transformation is not to be compared with either mechanism operating in the iron-nickel alloys. There are

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\* It should be noted that the Widmanstätten figure found in meteorites is generally assumed to have been formed during very slow cooling, that is, at a relatively high temperature, the occurrence of the Kurdjumow and Sachs relationship in the Cañon Diablo meteorite and the demonstration that this relationship obtains on transformation at high temperatures is confirmation of this assumption.



no data available on the crystallography of the transformation in iron-carbon alloys between the martensitic point and the pearlite point; the structures formed in this temperature range are acicular, resembling tempered martensite though not wholly<sup>16</sup>. Wever\* believes that a special reaction operates in this temperature range, a reaction leading to "cubic martensite." To complete the study of the mechanism of the  $\gamma$ - $\alpha$  transformation, this structure should be studied.

If we assume, on the basis of the present results, that the Nishiyama mechanism invariably operates at a temperature lower than that at which the Kurdjumow and Sachs operates we might expect to find it in iron-carbon alloys—or perhaps more likely in alloy steels—at temperatures lying below the martensite point, forming a second martensite point, and giving the "S-curve" three points of maximum reaction rate rather than two. Although temperatures in the neighborhood of  $-195^{\circ}$  are required to induce the Nishiyama mechanism in alloys with about 30 per cent Ni, it is possible that this mechanism might occur at higher temperatures in other alloys, and perhaps occur even during ordinary heat-treatment.†

The atomic matching on the composition planes in the  $\gamma$  and  $\alpha$  phases in the Kurdjumow and Sachs relationship does not differ appreciably from that in the Nishiyama relationship, and thus atomic matching is of no use in attempting to understand the occurrence of one or the other of the two mechanisms. There is, however, an important difference in the type of shear in the two mechanisms. Nishiyama recognized that the shear required by his relationship—shear in the [211] direction—is the same as that which occurs in twinning, and that the primary shear required by the Kurdjumow and Sachs relationship—shear in the [110] direction—is that which accompanies deformation by slip. It may be generally true that deformation is chiefly by slip at high temperatures and by twinning at low temperatures<sup>18</sup>, and that the operation chosen is the one that requires the lowest resolved shear stress at the temperature in question. If this be accepted, the selection of the Kurdjumow and Sachs relationship at high temperatures and the Nishiyama relationship at low temperatures becomes explicable, though the explanation is necessarily highly speculative.

### SUMMARY

1. The orientations of the  $\alpha$ -phase in a meteorite with 7 per cent Ni and in iron-nickel alloys containing from 27 to 31 per cent Ni which have

\* See summary in ref. 8, p. 87 ff.

† A. B. Greninger has reported<sup>17</sup> that  $\beta$ -brass forms on  $\alpha$  by the peritectic reaction according to the relationship of Nishiyama. Although this is a high-temperature reaction, the formation of  $\beta$  from the melt does not depend upon shearing processes, and this is a special type of transformation, which should be distinguished from those occurring entirely in the solid state.

been transformed above room temperature can be described by the relationship of Kurdjumow and Sachs:

$$\begin{array}{l} (111)_{\gamma} // (110)_{\alpha} \\ [110]_{\gamma} // [111]_{\alpha} \end{array}$$

2. The orientations of the  $\alpha$ -phase in iron alloys containing from 28.5 to 34 per cent Ni, which have been transformed at  $-190^{\circ}$ , can be described by the relationship of Nishiyama:

$$\begin{array}{l} (111)_{\gamma} // (110)_{\alpha} \\ [211]_{\gamma} // [110]_{\alpha} \end{array}$$

3. The orientations of the  $\alpha$ -phase in iron alloys containing 31 per cent Ni range between those predicted by Kurdjumow and Sachs and by Nishiyama when transformed at  $-70^{\circ}$  C.

4. The temperature of transformation rather than the alloy composition or the occurrence of transitional lattices determines which mechanism shall operate. In the alloys studied in this investigation the Kurdjumow and Sachs mechanism operates at high temperatures and the Nishiyama mechanism operates at low temperatures.

#### ACKNOWLEDGMENTS

Mr. A. R. Kommel assisted in this work by preparing the specimens and performing the metallographic work, and Dr. C. S. Barrett also by freely offering his advice and criticism.

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## DISCUSSION

(*Leland R. Van Wert presiding*)

L. W. McKEEHAN,\* New Haven, Conn.—One thing that bothered me in reading and listening to this paper was the rather complicated set of symbols used to designate the two possibilities. I should like, if it could be managed, to devise a set of words that would describe these two briefly. If we consider the close-packed planes in the last two lattices, the first statement in each case is equivalent to saying all close-packed planes are parallel. If we consider close-packed lines in those planes, the first statement is equivalent to saying that close-packed lines are parallel and the second that they are perpendicular, so that a possible shorthand for the two cases is parallel-parallel (meaning close-packed planes are parallel and close-packed lines in those planes are likewise parallel) and parallel-perpendicular, with the same sort of signification. Naturally, this simplification would not always work, but I think in this case, with all due respect to those whom the authors honored by the use of their names, it is easier to remember two orientations by a description of them, brief though it is, than by the names of the authors responsible for their description.

Another thing that worried me was the pole figures showing the orientation of the kamacite in the second part of the paper. In the first part, a picture was shown in which all the data had been compressed in one of the triangles bounded by three characteristic directions, and in the latter part of the paper the data were spread over six such triangles. I think it would be better to convert all those data into one such triangle, so as to make the population of points higher at the critical regions. There is another difficulty with diagrams like these, which is no fault of the authors', and merely should be called to the attention of those unfamiliar with them. If a pole figure has a boundary—in other words, is a partial figure—points will not cross that boundary; they will lie all on one side of it, and similarly at a corner, so that if we have an acute angle marked 111, all the points in the neighborhood must lie in this angle. This, of course, does not mean that they deviate all in one sense from the preferred position.

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\* Director, Sloane Physics Laboratory, Yale University.

A. B. GRENINGER,\* Cambridge, Mass. (written discussion).—I was considerably surprised to see the back-reflection Laue pattern shown in Fig. 1. The authors state that that photograph is typical of all the photographs of kamacite which they obtained. It seems remarkable that different pieces of the same meteoric fall would vary so greatly in the perfection of their structure, and if that is an established point, I think it is quite important because the Cañon Diablo fall was a cluster fall, I believe; that is, a large number of fragments fell at the same time. The fragments of this same fall that I have examined are very imperfect in structure. It seems possible, then, that the general scatter that is so prevalent in meteorites—it is a general rule, in fact, rather than the exception, for the kamacite to be highly scattered—may be produced by the impact of the meteorites when striking the earth. I think that can be verified; if it can, it will be a very important addition to the knowledge we have of meteorites.

I do not believe that the metallographic history of a meteorite can be described in such simple terms as the authors have used, although it does seem that from an orientation point of view we are dealing with a simple ex-solution of kamacite from taenite. However, there are other factors that should not be ignored. For instance, a large part of the life span of a meteorite is spent at absolute zero in its travel in interstellar space, and it is difficult to see how any taenite could be retained at such temperatures, which would necessarily have to occur if the kamacite precipitates from taenite at high temperature. I should also like to know what the authors think of Vogel's<sup>19</sup> contention that meteorites must be considered as ternary alloys of iron, nickel and phosphorous, and the gross structure—that is, the kamacite banding—represents a primary crystallization structure. It is at once obvious, of course, that it is difficult to reconcile this hypothesis or conclusion of Vogel's with the orientation relationships, but it is also difficult to reconcile the metallography of meteorites with the metallography of the artificial compounds of iron, nickel and phosphorous, unless this first assumption is made.

Another point that is quite important is the conclusion that different Widmanstätten mechanisms may operate at different temperatures. I do not believe, however, that the possibility of transition lattices has been eliminated. The reason I mention the point is that during the past year or two there has been so much attention directed to transition lattices and metastable diagrams, particularly in Germany and the Kurdjumow laboratory in Russia. There are also a few instances in recent Institute publications where it has been found that the precipitating phase is often quite different from the "stable" phase at that composition and temperature. For instance, the copper-zinc system has received probably more attention than any other alloy system, yet it was about six months ago that the first transition lattice was discovered, in the Kurdjumow laboratory—a tetragonal phase occurring between the body-centered and the face-centered cubic phases, and maintainable only at temperatures below zero.

We have devoted considerable time and study to this transformation in brass. The structure shown in Fig. 13 is a 60-40 copper-zinc alloy quenched from the beta range to room temperature, and further cooled to 50° below zero in a special, low-temperature microscope stage. On cooling, the markings begin to appear. Fig. 14 illustrates the same specimen cooled to about 100° below zero. It is possible to watch this transformation (through the microscope) and to observe the change that occurs as the temperature is lowered. There are at least three steps in the structural change, and at the very lowest temperatures the structure resembles martensite greatly.

\* Instructor in Metallurgy, Harvard University.

<sup>19</sup> R. Vogel: *Abhandl. der Ges. d. Wiss. zu Göttingen, Math.-Phys. K.L.* (1932) 3, pt. 6, 1-31.

Upon warming to room temperature, the entire structure disappears and the beta grains are as perfect as they were to start with. It is apparent that the copper-zinc and the iron-nickel diagrams are quite similar on the left-hand side, and of course it does not follow that there must therefore be a low-temperature tetragonal transformation in iron-nickel. But I believe there is a very good possibility of finding a tetragonal phase or some other transition phase in the iron-nickel system at low temperatures.

Another possible complicating factor is the order-disorder change, which may or may not occur in the iron-nickel transformation. It does seem somewhat paradoxical

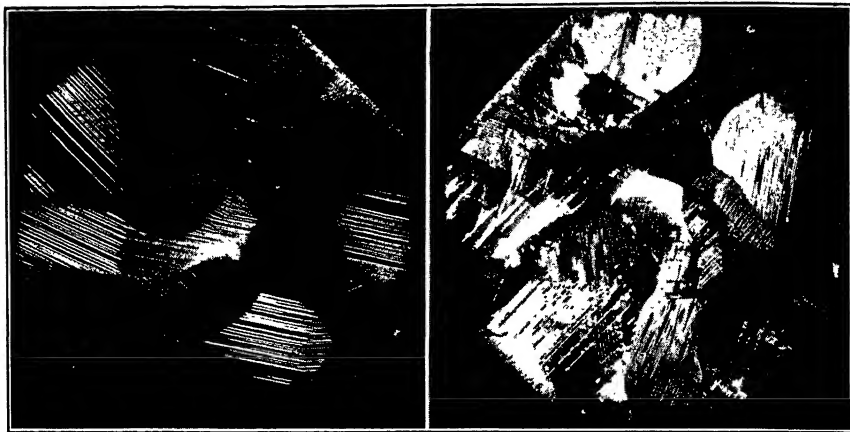


FIG. 13.

FIG. 14.

FIG. 13.—60-40 COPPER-ZINC ALLOY.

Quenched from 860° C. to room temperature, and further cooled (slowly) to about -50° C. and photographed at that temperature.

FIG. 14.—SPECIMEN OF FIG. 13 FURTHER COOLED TO ABOUT -100° C. AND PHOTOGRAPHED AT THAT TEMPERATURE.

Original magnification 15; reduced  $\frac{1}{4}$  in reproduction. Oblique illumination.

that in the two systems from which we have obtained most of our data on transformations (the iron-nickel and the copper-zinc) it is very difficult, yet not quite impossible, to distinguish between order and disorder by X-ray means.

However, there is one interesting example of a transformation in which we know order-disorder takes place—the interesting work of Graf<sup>20</sup> on the copper-palladium system. Graf's relationships between the face-centered cubic lattice and the body-centered cubic lattice are quite different from those between similar lattices in other systems. Graf's relationship is as follows:

$$\begin{array}{l} (001)_{\alpha} // (113)_{\beta} \\ [311]_{\alpha} // [100]_{\beta} \end{array}$$

This relationship is approximately the same as that which would obtain if the two lattices were placed parallel and one were rotated 30° about the threefold axis; that is, one-fourth of the distance required for a symmetry operation.

I think, then, that tentatively, although the authors are quite justified in concluding that transformation mechanism may be different at different temperatures, it is

<sup>20</sup> L. Graf: Kinetik und Mechanismus der Allotropen Umwandlung im System Palladium-Kupfer. *Physik. Ztsch.* (1935) No. 14, 489-498.

not wise to disregard or eliminate the possible influence that a transition lattice or an order-disorder change may have on the mechanism.

G. SACHS,\* Newark, N. J.—What is the real difference between the martensitic structure and the Widmanstätten structure? Also, is there any gradual change from one structure to the other? Considering, for instance, alpha-beta brass, which develops structures very similar to steel, there seems to be a gradual change from one type of structure at low tempering temperatures to another at high temperatures. At low temperatures there is a very regular structure, which resembles that of martensite; and the chief characteristic of this structure seems to be that the crystals of the new phase develop at once to their finished size, and that the continuous transition gives more and more of such crystals but does not change the size of these new crystals. But at somewhat higher temperatures, the first formed crystals are also very regular, but later on they grow in size and become irregular. It seems to me that the martensitic structure of steel is somewhat similar in that respect, as the crystals develop at once to their finished size whereas the Widmanstätten structure seems to be a crystallographically grown structure.

L. W. MCKEEHAN.—I should like to revise one of my statements before Dr. Mehl takes it to pieces. Instead of such a simple description as "parallel-parallel," or "parallel-perpendicular," I should like to change it to "parallel-closest-parallel," or "parallel-next-to-closest-perpendicular."

G. DERGE.—We all appreciate, of course, Professor McKeehan's attempt to simplify the nomenclature, but I am afraid he has almost defeated his own purposes. It certainly would be pleasant if some simple way of describing various orientation relationships could be devised.

R. F. MEHL AND G. DERGE (written discussion).—The properties of pole figures and unit stereographic triangles, which Professor McKeehan has pointed out, should always be kept in mind. However, we still prefer to record the data as in the paper. Where unit triangles have been used a large number of experimental points are being considered statistically and should therefore be concentrated as much as possible. Where quadrants are used, no attempt has been made at a statistical treatment, each individual point bears full weight, and we feel that the more complete symmetry of the quadrant helps one visualize the meaning of these data. The ultimate result is the same by either treatment.

Regarding Dr. Greninger's remarks, it is true that the back-reflection Laue photograph of Fig. 1 is a typical pattern. Films from about 50 different kamacite lamellae have been made and only two or three of these show an appreciably greater degree of imperfection.

We studied a section of the Amalia Farms fall, South Africa, and found it to be highly imperfect. A short paper comparing the structures of the Cañon Diablo and Amalia Farms specimens will be published soon in the *American Journal of Science*. Research with modern metallurgical methods undoubtedly would reveal a good deal about the past history of meteorites.

A detailed discussion of the numerous speculations that have already been proposed by metallurgists would require a good deal of time. Vogel's suggestion is among the most interesting. Dr. Greninger has already suggested one of the strongest arguments against it. In addition, analysis has shown that taenite usually contains 34 per cent nickel or more and work on pure iron-nickel alloys has established very definitely that the gamma to alpha transformation is infinitely slow in alloys containing more

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\* Baker & Co., Inc.

than 34 per cent nickel. The fact that taenite has been retained, even at absolute zero, for aeons of time can be explained by the simple iron-nickel diagram by this reasoning.

The possibility that the transformation mechanism has been altered by transition lattices that occur only at low temperatures cannot be denied. However, such lattices have been sought very carefully in 30 per cent alloys with only negative results.<sup>14</sup> Whether or not such lattices exist, our contention that the transformation mechanism is different at different temperatures is not altered.

Dr. Sachs' questions as to the real difference between "martensitic" and "Widmanstätten" structures and whether the transition between them is sharp or gradual are important questions, which physical metallurgists will have to answer sooner or later. We hope to do more work on these problems in our laboratory. At least a partial answer will be furnished when the eutectoid decomposition of a steel is studied crystallographically throughout the entire temperature range over which the reaction operates.

The interest in this paper speaks well for the advantages of this type of research. The original problem was a crystallographic study of the transformation in an iron-nickel alloy. From this study information was obtained which has been applied to the purely philosophical subject of the history of meteorites and to the extremely practical subject of the reactions involved in heat-treating steel.

## Preferred Orientations Produced by Recrystallizing Cold-rolled Low-carbon Sheet Steel

BY M. GENSAMER\* AND B. LUSTMAN,† MEMBERS A.I.M.E.

(Cleveland Meeting, October, 1936)

A RECENT paper<sup>1</sup> described, by means of stereographic pole figures, the preferred orientations produced by cold-rolling low-carbon steel of automobile-body grade. It was found that the surface of the sheet exhibited a deformation texture significantly different from the texture possessed by the inside of the sheet. Efforts to produce the surface texture by buffing a sample exhibiting the normal or inside texture, using a copper lap, have not been successful. In view of the data collected by Kurdjumow and Sachs<sup>2</sup>, it was suggested that the surface texture might be the result of partial recrystallization of the normal or inside texture. The recrystallization texture of cold-rolled mild steel was studied by Goss<sup>3</sup>, but he did not use the pole-figure method, so that his conclusions were in need of verification. For these reasons the work reported in here was undertaken. It had two objectives: (1) to study the general behavior of cold-rolled mild steel on recrystallization below the critical temperature  $A_1$ , and (2) to attempt experimentally a demonstration of the genesis suggested above for the surface texture in cold-rolled steel.

The material was that used by Gensamer and Mehl, cold-rolled to 97.5 per cent reduction in thickness. Fig. 1 is an X-ray pinhole photograph of this material, taken with the beam transmitted perpendicular to the plane of the sheet, using a molybdenum target at 35 kv. with no filter. It is typical of the inside texture, but in it the deformation texture is better developed than in the samples that showed a well developed difference between the inside and surface samples. Specimens from this sheet, which was 0.005 in. thick, were annealed for 5 min. at various temperatures in a lead bath. After about 0.0005 in. had been etched from both surfaces, X-ray photograms were prepared, using the technique described in the earlier paper<sup>1</sup>.

Figs. 2 to 6 are photograms of the annealed sheet, at 566, 571, 577, 580 and 650° C. (1050° to 1202° F.), in order. Fig. 2 shows that 5 min.

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<sup>1</sup>References are at the end of the paper.



at 566° C. produced little change in the cold-rolling texture (photograms taken with the beam perpendicular to the plane of the sheet have been demonstrated to be most sensitive to the differences in texture produced by annealing and to the differences between the inside and the surface of the cold-rolled sheet). Fig. 3, for annealing 5 min. at 571° C., shows

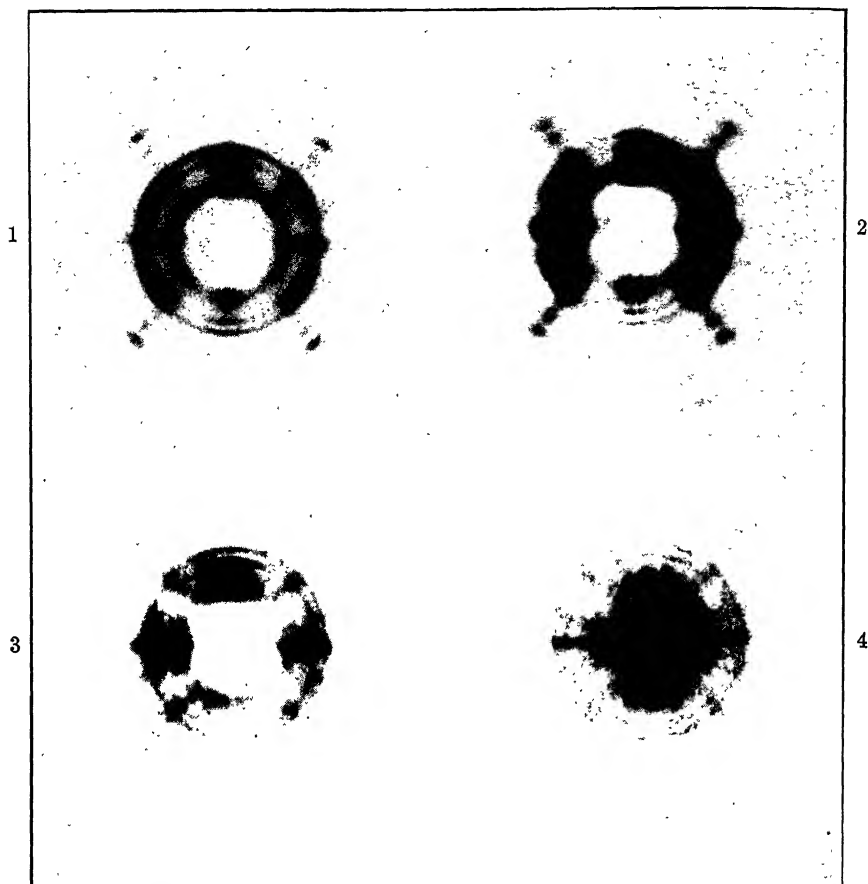


FIG. 1.—X-RAY PHOTOGRAPH OF INSIDE OF SHEET. SAMPLE REDUCED 97.5 PER CENT BY COLD-ROLLING. NO ANNEAL.

FIG. 2.—SAME MATERIAL, ANNEALED 5 MINUTES AT 566° C.

FIG. 3.—SAME MATERIAL, ANNEALED 5 MINUTES AT 571° C.

FIG. 4.—SAME MATERIAL, ANNEALED 5 MINUTES AT 577° C.

some difference. In Fig. 4, for 577° C., this difference is better developed, and in Fig. 5 for 580° C. still better. Higher temperatures produced a gradual change culminating in the texture represented in Fig. 6, for 650° C., which shows an almost complete elimination of features typical of the cold-rolled material and the development of a quite new texture, the tendency toward which is discernible as far back as 571° C. (Fig. 3).

Photomicrographs were prepared from these specimens, and may be compared with the original material, cold-worked 97.5 per cent (Fig. 7). They show that some recrystallization occurred at 566° C. (Fig. 8) and was well developed at 580° C. (Fig. 9), although apparently not complete. At 650° C. (Fig. 10) recrystallization seems complete. Thus there is a nice correlation between the evidence of the X-ray method and microscopy concerning the progress of recrystallization, which of course has been shown before.

There is no evidence for a completely random structure on recrystallization at low temperatures, followed by the development of a recrystallization texture at higher temperatures, as suggested by Goss<sup>3</sup>. In the work reported here a well developed texture exists at all temperatures

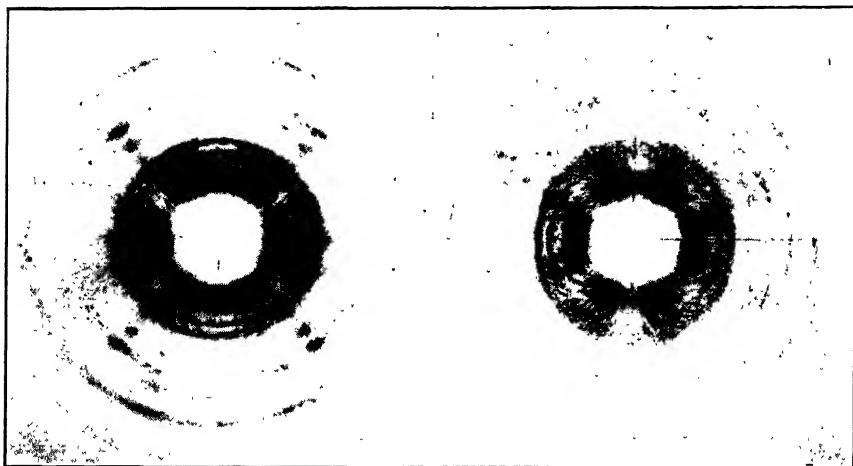


FIG. 5.

FIG. 6.

FIG. 5.—SAME MATERIAL AS FIG. 1, ANNEALED 5 MINUTES AT 580° C.

FIG. 6.—SAME MATERIAL, ANNEALED 5 MINUTES AT 650° C.

below the critical  $A_1$ . The deformation and recrystallization textures are significantly different. Whether sheets possessing these different textures exhibit significant differences in anisotropy of mechanical properties has not yet been studied.

None of the X-ray photograms produced may be considered to do more than resemble those for the surface texture of the cold-rolled sheet. But if allowance is made for the expected difference in grain size between the material recrystallized in the lead bath and the cold-rolled specimens (as shown by the relative size of the individual diffraction spots in the photograms), this resemblance is reasonable. If it could be shown through pole figures that the textures developed are the same, the second objective in this work might be considered accomplished.

Stereographic pole figures were prepared for the samples annealed at 580° and 650° C. All the pole figures in this paper are for the  $\{110\}$

planes, with the plane of the sheet as the projection plane and with the rolling direction vertical. Fig. 11 is a  $\{110\}$  pole figure for the sample that was partly recrystallized by annealing for 5 min. at  $580^{\circ}\text{C.}$ , for which temperature the photogram (Fig. 5) most nearly resembled that

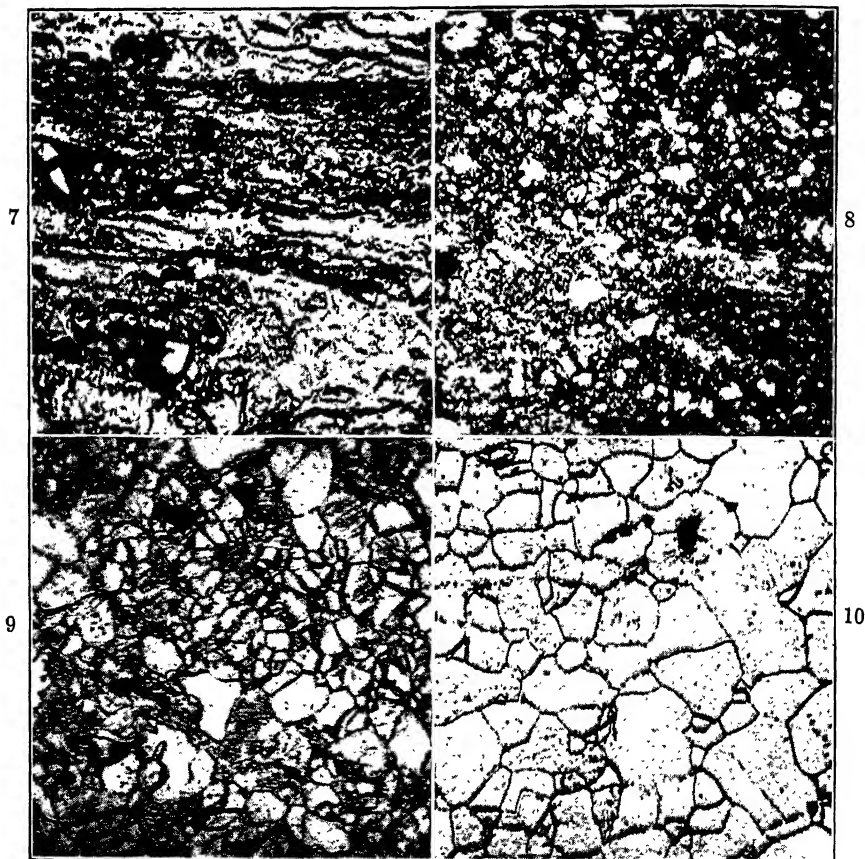


FIG. 7.—SAMPLE REDUCED 97.5 PER CENT BY COLD-ROLLING, NO ANNEAL.

FIG. 8.—SAME MATERIAL, ANNEALED 5 MINUTES AT  $566^{\circ}\text{C.}$

FIG. 9.—SAME MATERIAL, ANNEALED 5 MINUTES AT  $580^{\circ}\text{C.}$

FIG. 10.—SAME MATERIAL, ANNEALED 5 MINUTES AT  $650^{\circ}\text{C.}$

All  $\times 500$ .

for the surface texture in cold-rolled sheet. For comparison, the  $\{110\}$  pole figure for this surface texture has been reproduced from the earlier paper<sup>1</sup>, and is shown in Fig. 12, showing that the two pole figures are similar.

Fig. 13 is a  $\{110\}$  pole figure for the sample annealed at  $650^{\circ}\text{C.}$  and apparently completely recrystallized. Fig. 14 is reproduced from the work of Kurdjumow and Sachs<sup>2</sup>, for comparison, and shows essentially the same result for electrolytic iron sheets; this texture was characteristic

of samples recrystallized at any temperature below  $840^{\circ}\text{C}$ . It should be noted that the recrystallization texture (Figs. 13 and 14) may be

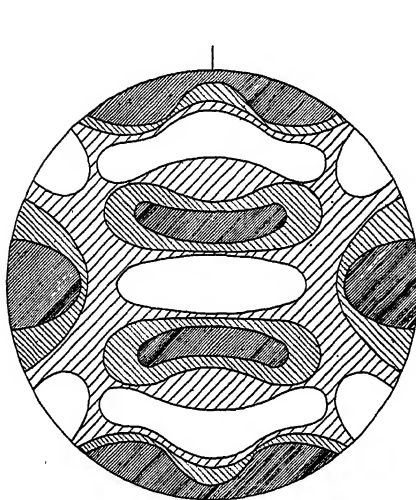


Fig. 11.

Fig. 11.— $\{110\}$  POLE FIGURE, MILD STEEL COLD-ROLLED 97.5 PER CENT, ANNEALED 5 MINUTES AT  $580^{\circ}\text{C}$ .

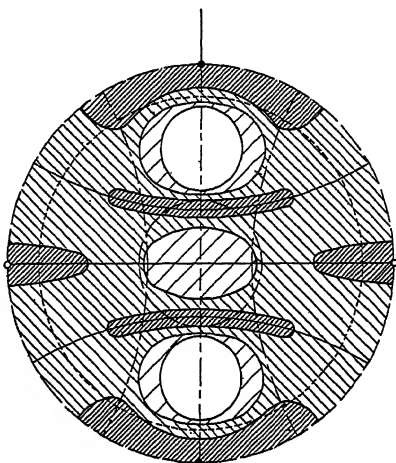


Fig. 12.

Fig. 12.— $\{110\}$  POLE FIGURE, SURFACE TEXTURE OF MILD STEEL COLD-ROLLED 85 PER CENT, NO ANNEAL.

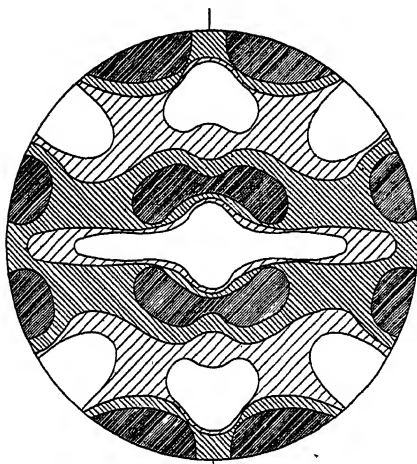


Fig. 13.

Fig. 13.— $\{110\}$  POLE FIGURE, MILD STEEL COLD-ROLLED 97.5 PER CENT, ANNEALED 5 MINUTES AT  $650^{\circ}\text{C}$ .

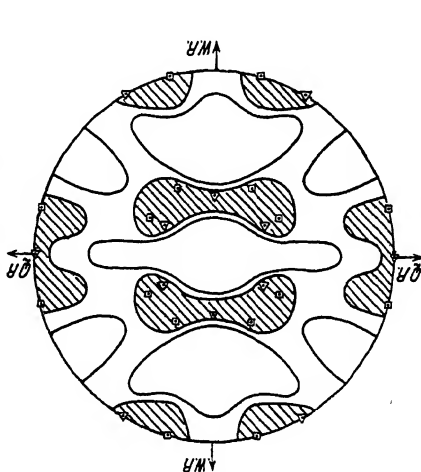


Fig. 14.

Fig. 14.— $\{110\}$  POLE FIGURE OF KURDJUMOW AND SACHS, ELECTROLYTIC IRON COLD-ROLLED 98.5 PER CENT, RECRYSTALLIZED BELOW  $840^{\circ}\text{C}$ .

considered to be derived from the deformation texture (Fig. 15 of the earlier paper<sup>1</sup>) by rotations of  $15^{\circ}$  both clockwise and counterclockwise

about the normal to the plane of the sheet, which is predominantly a [100] direction. This is in agreement with the work of Glocker<sup>4</sup>, but is not in agreement with the conclusion of Goss<sup>3</sup> that the two coexistent ideal orientations are related as are the parent crystal and its mechanical twin in the deformation twinning of alpha iron (Neumann band formation). This twinning relation requires a rotation of 60° about a [111] direction, which is not consistent with the pole figures presented here. If the twinning mechanism plays any part in the genesis of the recrystallization texture in iron, that part is still obscure.

### SUMMARY

From the data presented, the following conclusions seem justified:

1. Cold-rolled mild steel exhibiting a well developed deformation texture recrystallizes with the formation of a recrystallization texture.
2. At no temperature of recrystallization below the critical is there produced a random orientation of the crystallites (725° C. was the highest used in this work, but 840° C. was used by Kurdjumow and Sachs<sup>2</sup>).
3. Glocker's<sup>4</sup> relationship between the deformation and recrystallization textures has again been substantiated, but no rationalization of the process is offered at this time.
4. The pole figure for partly recrystallized cold-rolled mild steel agrees well enough with the pole figure for the surface of cold-rolled samples to lend support to the hypothesis that the surface texture may be produced by partial recrystallization of the texture characteristic of the inside of the sheet.

### ACKNOWLEDGMENT

This work was performed partly as a senior thesis in the Department of Metallurgy and partly as a research project in the Metals Research Laboratory at the Carnegie Institute of Technology in Pittsburgh, Pennsylvania, under the direction of R. F. Mehl.

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3. N. P. Goss: *Trans. Amer. Soc. Steel Treat.* (Sept., 1929) **16**, No. 3, 405-414.
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### DISCUSSION

[For discussion see page 511]

## Preferred Orientations in Hot-rolled Low-carbon Steel

BY M. GENSAMER\* AND P. A. VUKMANIC,† MEMBERS A.I.M.E.

(Cleveland Meeting, October, 1936)

ONLY recently has it been realized that preferred orientations are common in hot-rolled steels. In a recent paper, N. P. Goss<sup>1</sup> stated that hot-rolled mild steel exhibits a texture different from that characteristic of cold-rolled steel. No complete study of these hot-rolling textures has been reported using the pole-figure method of Wever.

The material used in the work reported in this paper was the same material used by Gensamer and Mehl<sup>2</sup> in a recent study of preferred orientations in cold-rolled steel, to which reference may be made for the composition and thermal history of the steel. Automobile-body sheet bar  $\frac{1}{4}$  in. thick was hot-rolled at two temperatures, 780° and 910° C. (1436° and 1669° F.). These temperatures refer to the temperature of the furnace in which the steel was heated; after each pass the steel was returned to the furnace and held there long enough to return to temperature. Although no accurate method was used to measure the temperature after each pass, it was estimated by color that only a slight drop in temperature occurred. In order to determine the effect of any preferred orientation that might have persisted through the normalizing treatment, one specimen at each temperature was rolled in the same direction as the original working direction and the other at right angles to it. The total reduction in each case was 85 per cent, the specimens having been reduced from 0.250 to 0.0375 in. in five passes. Final cooling was in air.

Pinhole reflection photograms were taken of all four specimens, with the rolling direction vertical and the X-ray beam at an angle of 7° with the transverse direction (the transverse direction is defined as that direction in the rolling plane perpendicular to the rolling direction). These photograms, taken with a Mo target at 35 kv., are reproduced in Figs. 1, 2, 3 and 4. They show that a more pronounced texture was developed by the low-temperature rolling (780° C.), and that of the two

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<sup>1</sup> N. P. Goss: *Metals & Alloys* (1936) 7, No. 5, 131-134.

<sup>2</sup> M. Gensamer and R. F. Mehl: *Trans. A.I.M.E.* (1936) 120, 277.

samples rolled at this temperature the one rolled parallel to the original working direction exhibited the better developed texture. This specimen was used in deriving the pole figure described below. Fig. 5 is another photogram of this specimen, taken by the transmission technique with the X-ray beam making an angle of  $20^\circ$  with the transverse direction and  $90^\circ$  with the rolling direction, and illustrating how well developed a texture exists in the steel rolled at this temperature ( $780^\circ\text{C}$ ). Fig. 6 is a similar photogram for the specimen rolled parallel to the original rolling direction at  $910^\circ\text{C}$ .

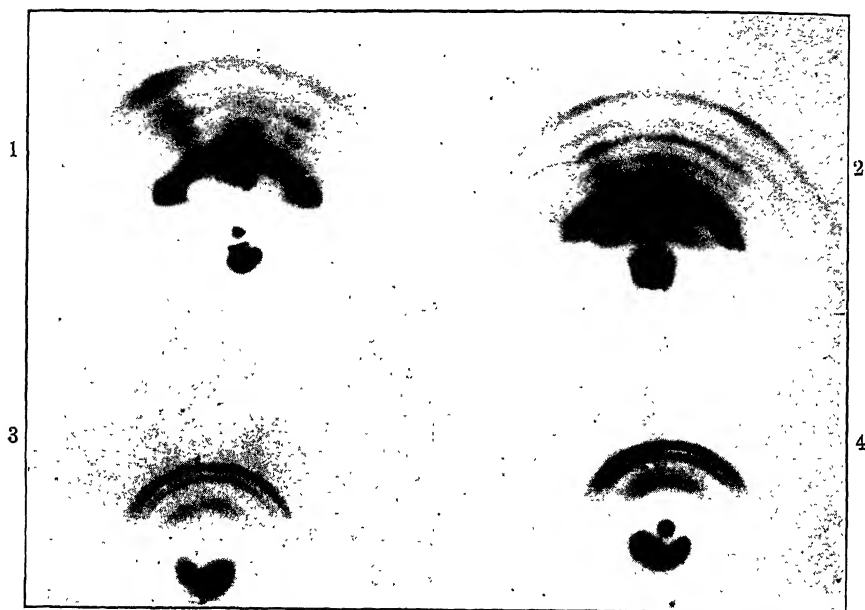


FIG. 1.—STEEL ROLLED AT  $780^\circ\text{C}$ . PARALLEL TO ORIGINAL WORKING DIRECTION.  
 FIG. 2.—STEEL ROLLED AT  $780^\circ\text{C}$ . PERPENDICULAR TO ORIGINAL WORKING DIRECTION.  
 FIG. 3.—STEEL ROLLED AT  $910^\circ\text{C}$ . PARALLEL TO ORIGINAL WORKING DIRECTION.  
 FIG. 4.—STEEL ROLLED AT  $910^\circ\text{C}$ . PERPENDICULAR TO ORIGINAL WORKING DIRECTION.

Fig. 7 is a photomicrograph of the specimen rolled parallel to the original working direction at  $780^\circ\text{C}$ . Fig. 8 is the  $\{110\}$  pole figure prepared from this specimen; the plane of the sheet is the projection plane, and the rolling direction is vertical. The specimen was coarse grained (about 200 grains per sq. mm.). As a result the photograms taken with the beam nearly perpendicular to the sheet were spotty and difficult to interpret. For this reason some of the regions on the pole figure are indicated by dotted lines. The more heavily shaded of these regions are clearly required by symmetry considerations and agree well with the data from the photograms, but the evidence for the lighter regions within the dotted lines is less positive.

The pole figure derived resembles those obtained for cold-rolled mild steel, as exemplified by Fig. 9, which is taken from the work of Gensamer

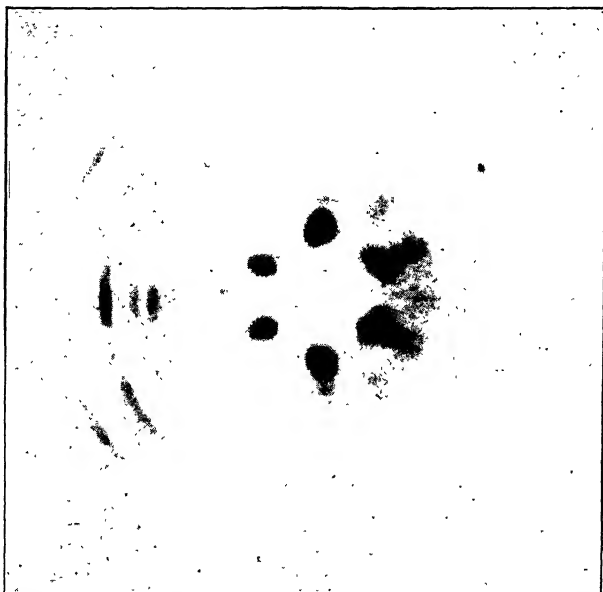


FIG. 5.—STEEL ROLLED AT 780° C. PARALLEL TO ORIGINAL WORKING DIRECTION.

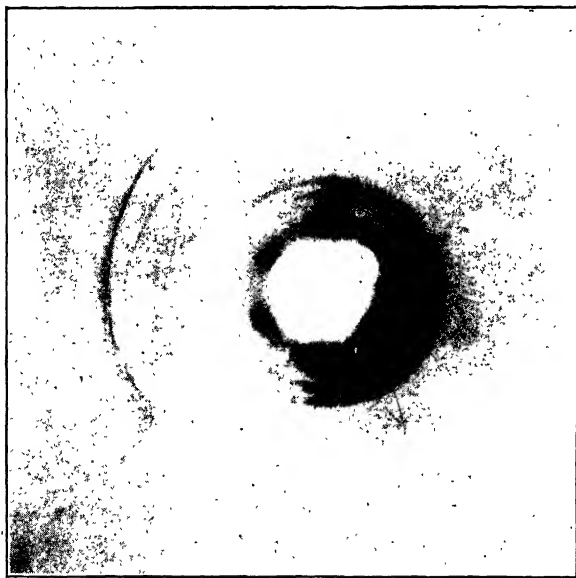


FIG. 6.—STEEL ROLLED AT 910° C. PARALLEL TO ORIGINAL WORKING DIRECTION.

and Mehl<sup>2</sup>. It is not surprising that the pole figures are similar, for we have no reason to believe that the crystallographic mechanism of deforma-



tion for alpha iron is different at elevated temperatures<sup>3</sup>; and even though new grains formed by recrystallization at the working temperature should



FIG. 7.—STEEL ROLLED AT 780° C. PARALLEL TO ORIGINAL WORKING DIRECTION.  $\times 200$ .

assume orientations consistent with the recrystallization texture reported by Gensamer and Lustman<sup>4</sup>, these new grains when re-rolled should promptly change their orientations by the same kind of rotations experienced in cold-rolling. It might be pointed out that this view is hardly consistent with the suggestion advanced by Gensamer and Mehl to account for the surface texture of cold-rolled steel. It might also be pointed out that the results of this work do not confirm the statement of Goss already referred to<sup>1</sup>; the hot-rolling and cold-rolling textures observed in this work are very similar.

No pole figure was prepared for the steel rolled at 910°. The texture

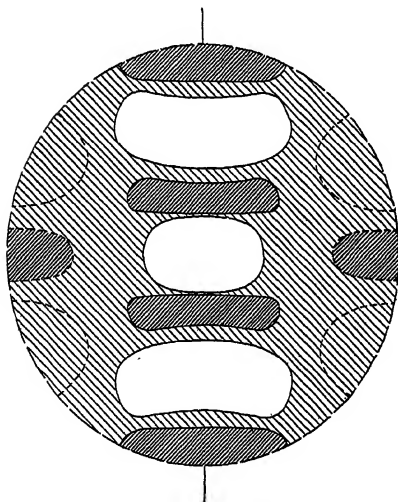


FIG. 8.—{110} POLE FIGURE FOR MILD STEEL ROLLED 85 PER CENT AT 780° C.

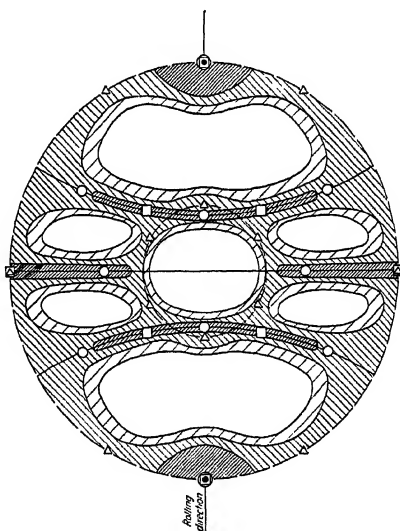


FIG. 9.—{110} POLE FIGURE FOR MILD STEEL COLD-ROLLED 99 PER CENT.

was hardly well enough developed, and indeed might have been inherited

<sup>3</sup> C. S. Barrett, G. Ansel and R. F. Mehl: Slip, Twinning and Cleavage in Iron and Silicon Ferrite. Amer. Soc. Metals Preprint, Cleveland Meeting, 1936.

<sup>4</sup> M. Gensamer and B. Lustman: This volume.

from earlier rolling processes rather than developed during this rolling. It is well known that rolling textures may persist through annealing, and it is feared that such may have happened in these experiments, for the 910° C. texture was better developed in the sample rolled parallel to the original rolling direction than in the one rolled transverse to this direction. Also, it is not quite certain that the temperature remained above the  $A_3$  critical temperature, so that the steel may have been deformed in the alpha condition rather than in the gamma, as was intended. Further experiments concerned with the effect of the phase change and rolling above the critical temperature are contemplated.

### SUMMARY

1. Mild steel rolled at 780° C. exhibits well developed preferred orientations.

2. Mild steel rolled at 910° C. exhibits a much less well developed texture.

3. The texture developed at 780° C. closely resembles the texture developed by cold-rolling. This texture has been described by a stereographic pole figure.

### ACKNOWLEDGMENT

This work was performed partly as a senior thesis in the Department of Metallurgy and partly as a research project in the Metals Research Laboratory at the Carnegie Institute of Technology in Pittsburgh, Pennsylvania, under the direction of R. F. Mehl.

### DISCUSSION

*(Kent R. Van Horn presiding)*

(This discussion refers also to the paper by M. Gensamer and B. Lustman, beginning on page 50)

K. R. VAN HORN,\* Cleveland, Ohio.—The authors have reported that the type of preferred grain orientation in the interior of the sheet is different from that in the surface. Could these variations be attributable to the conditions of rolling—such factors as the roll diameter, roll pressure, tension applied to the sheet, rolling temperature, etc.—rather than the possibility of recrystallization? The effects of these rolling factors on grain orientation have received relatively little consideration. Many reports of the X-ray analysis of grain orientation in rolled products give no data on rolling procedure, and assume that the observed type of grain alignment is characteristic for the rolling process of the metal under investigation. Possibly the various types of preferred orientation obtained by rolling one metal might be explained if the rolling conditions of the various investigations were known. Certainly more exhaustive studies of these rolling factors should be initiated.

Recently Prof. W. P. Davey, of Pennsylvania State College, made a notable start in investigating some of these factors. The results of a part of this study were

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\* Aluminum Company of America.

presented at the X-ray Session of the American Society for Metals.<sup>5</sup> The authors studied the effects of the percentage of reduction per pass, rolling temperature, and concentration of nickel in binary iron-nickel alloys on the type of preferred grain orientation produced during rolling. Although they found that these three factors seemed to have little influence on the type or degree of grain alignment, it is possible that variations in roll diameter and size and roll pressures may be important. Small rolls and roll pressures tend to effect the reduction during rolling by tension or a drawing action; and, in fact, sheet may be reduced entirely by tension. Large rolls and heavy roll pressures tend to reduce sheet by compression, and this condition would approximate a pressing or forging operation. It is to be expected that different types of preferred orientation would result when sheet is rolled under these two widely different conditions. Perhaps some of these factors might cause the variations in grain alignment observed by Messrs. Gensamer and Lustman.

R. H. HOBROCK,\* Detroit, Mich.—Recrystallization is thought to require some minimum temperature, which for low-carbon steel is rather high. If I understand correctly, the author proposes to explain the difference between the orientations on the exterior and the interior of the sheet by proposing that the exterior had recrystallized during cold-rolling. If the energy to raise the temperature to the recrystallization temperature is derived from the plastic deformation of the metal during the rolling, it should be possible by considering the energy expended on the metal and the mass and specific heat of the metal to roughly arrive at a temperature value the metal might achieve. Has such an approximation been made? Or does the author believe that recrystallization can occur at quite a low temperature during the course of plastic deformation?

N. P. GOSS,† Youngstown, Ohio (written discussion‡).—Gensamer and Lustman believe that recrystallization and deformation textures can only be completely determined by the pole-figure method, as originally developed by Franz Wever. In my paper a different method was used, therefore the authors felt that my conclusions needed verification. I am not convinced that the pole-figure method is the only one possible, for it is easy to demonstrate that simpler methods based on some form of model representation is much easier to visualize and understand. The average metallurgist is not familiar with the pole-figure method and cannot picture just how the lattice cells are oriented and distributed in space. A model showing the ideal orientations present, and accompanied either by a set of distribution curves or a suitable table showing the deviations from the ideal orientations, assumed under various conditions of working, heat-treatment, etc., would certainly be much easier to understand and more effective. Also, it should be remembered that the X-ray analyst is always endeavoring to convince the metal-working industries of the importance and value of this method. I am sure that if the X-ray diffraction methods employed in metallurgical investigations could be explained as simply and clearly as Professor Sauveur has explained the metallography of iron and steel, greater usage of the method would certainly follow. It would be of interest to know how many metallurgists can interpret the pole figures shown in this paper. Would it not be helpful to have a model accompany the pole figure; i.e., showing the ideal orientation and the statistical distribution or deviation from the ideal?

I have used this method for many years, and I find that the metallurgist can under-

<sup>5</sup> W. P. Davey and D. A. McLachlan: An X-ray Study of Preferred Orientations in Pure Cold-Rolled Iron-Nickel Alloys. *Trans. Amer. Soc. Metals* (1937).

\* Research Laboratory, Bundy Tubing Co.

† Physicist, Cold Metal Process Co.

‡ This discussion refers to the paper beginning on page 501.

stand it. What interests the metallurgist is the possible effect of grain orientation on the physical properties of the metals, and the X-ray method is unique in showing a definite relationship between the physical properties and preferred orientation of the grain structure.

After all, the problem is to determine the orientations present and their distribution about the ideal, and their effect on the physical properties of the metals. That is the important thing, and the simpler the method of representation the better.

In discussing my work, the authors referred only to the first paper, published in 1929. Another paper was published in 1930.<sup>6</sup> Unfortunately, the authors did not know this. This paper showed that the new recrystallization texture is also developed below  $A_1$ . In repeating this experiment, the authors have drawn the same conclusions. I also found that the other type of recrystallization structure is possible but does not occur as frequently.

This recrystallization texture is developed only when the strip steel is given an area reduction in excess of 90 per cent. In a specimen given an area reduction of 98 per cent and heat-treated at 1000° F. the new recrystallization structure was found, but it was of interest to find that an annealing time of 15 min. did not completely recrystallize the cold-worked structure. A longer time was required to completely recrystallize it. (*Op. cit.*, Fig. 5, p. 1242.)

The authors find that annealing such strips at 1050° F. did not alter the cold-rolled texture. This is not surprising, since their annealing time was only 5 min. It would be interesting to see what effect longer time at temperature would have on their specimens. When I heat-treated my specimens at 1100° F. recrystallization diagrams similar to the one shown in Fig. 5 of Gensamer and Lustman's paper were obtained.

One thing the authors have shown very nicely is the correlation between the X-ray structure and the photomicrographs of corresponding specimens. The X-ray is unique in that it shows the orientation texture; the photomicrographs do not show this, but the microscope shows other details not revealed by the X-ray.

I do not believe the authors have demonstrated that this new orientation is not due to twinning on the {211} planes with the (211) planes in the rolling direction. Glocker's analysis from an analytical viewpoint is correct, but he did not attempt to explain why this unusual structure developed. I have attempted to explain it, and found that when the cold-worked structure recrystallized twinning occurred on the {211} planes, and the (211) plane tended to coincide with the direction of rolling. Here we have a recrystallization twin, instead of the familiar mechanical twin due to shock. I also found that the {211} planes and the {100} planes were strongly present in the surface, whereas the authors mention only the {100} plane as predominating.

I do not understand why twinning on {211} planes requires a rotation of 60° about a [111] direction.

K. R. VAN HORN.—In regard to Mr. Goss's remarks suggesting that annealing twins should occur in iron inasmuch as they are prevalent in annealed alpha brass, there appears to be some evidence why this should not be true. Alpha brass has a face-centered cubic crystal structure and, similar to most face-centered cubic metals, forms the familiar straight-sided bands or twins within the grains after deformation followed by annealing. Apparently deformation alone cannot produce the twin markings in face-centered cubic metals or alloys.

The hexagonal metals cadmium, magnesium and zinc form twins upon mechanical working or deformation. These twins have a spindle or acicular form, which is different in appearance from the annealing twin bands of the face-centered cubic metals. Deformed hexagonal metals do not form twin bands upon annealing.

Iron has a body-centered cubic structure and forms twins of the mechanical type and not the annealing type. This is typical of other body-centered metals. These

<sup>6</sup> N. P. Goss: *Trans. Amer. Soc. Steel Treat.* (July-Dec. 1930) 18.

twins are referred to as Neumann bands, and are produced by the deformation of iron. It would seem, therefore, that the type of twin formation is related to the crystal structure of the metal and that annealing twins are not characteristic of iron or body-centered metals.

N. P. Goss (written discussion).—Gensamer and Vukmanic in their paper point out that very little has been published on the X-ray structure of hot-rolled steels and metals in general. During the past 10 years numerous industrial laboratories have carried out rather extensive investigations on hot-rolled metals, but the results were never published for public consumption.

The specimens the authors used are not typical of commercial hot-rolled strip. Why did they not use the product of the continuous strip mills? These mills finish low-carbon steel above and below  $A_3$ , depending upon the requirements. The X-ray diagram shown in Fig. 6 (p. 509) is not representative of a hot-rolled strip finished above  $A_3$ . Such strips (low-carbon steel) are usually characterized by a structure in which the grains are oriented at random. This procedure is followed in commercial rolling to obtain a strip that will not ear when deep drawn. On the other hand, the structure shown in Fig. 5 (same page) is often found in low-carbon strip steels finished at  $780^\circ\text{C}$ ., allowed to cool freely in air; however, if the strip is coiled at this temperature, partial recrystallization and grain growth may occur. Fig. 5 would suggest that the  $\{211\}$  and  $\{100\}$  planes lie in the surface of the strip.

I found that the grain fragments in low-carbon hot-rolled and cold-rolled strip steels are oriented with the  $[110]$  direction in the direction of rolling, but the distribution of the lattice fragments or blocks varied considerably, depending upon the roll diameter, the amount of cold-rolling and hot-rolling above and below  $A_3$ . Grain size is still another important factor; however, the pole figures do not seem to show this very distinctly since they should show the distribution (variation) of the poles.

Another fact must also be considered; if the hot-rolled strip is free of preferred orientation, and is cold-rolled, the fiber structure will differ from that made of a cold-rolled hot strip, which had a strong fiber texture to start with. The distribution will certainly be different, if all the other experimental conditions are kept the same.

In hot-rolled rods, I found that the fiber structure is developed at right angles to the rod axis. (The reason for this is explained in the paper I have presented at this convention.) The reason for this "cross fiber," as I have termed it, in hot-rolled rods is easy to explain if one considers the manner in which a rod is rolled from a billet (see page 656, *Metals Hand Book*, 1936 Edition). The last pass is oval to round. The reduction along the major axis of the oval is large, i.e., the working of the rod from oval to round may be considered to be an upsetting operation, with the result that a cross fiber is developed, with the "cross-fiber axis" parallel to the axis of the work rolls of the hot mill. In a hard-drawn wire, the fiber structure is developed along the wire axis and at random about the axis.

The authors state that their results do not confirm mine, but they have confused hot-rolled strip textures with hot-rolled rod textures, to which they refer in my paper. Inasmuch as they did not study hot-rolled rod textures, in which I found the direction of "fiber axis" to differ from that of a cold-drawn wire, but in hot-rolled strips and in cold-reduced strip I found the fiber axis to coincide with the rolling direction, I therefore feel that the conclusions drawn by the authors in reference to my work are not justified.

M. GENSAMER, B. LUSTMAN AND P. A. VUKMANIC (written discussion).—We wish to thank Mr. Goss for his long discussion. We do not think that at a meeting devoted

<sup>1</sup> N. P. Goss: Hot Working, Cold Working and Recrystallization Structure. *Trans. Amer. Soc. Metals* (1936) 329.

entirely to X-ray crystallography we need to apologize for using a method of presenting crystallographic data which has been standard with all crystallographers for many years, both here and abroad. When we add to this that the stereographic pole-figure method is capable of representing all the data in a manner that is as simple and easy to understand as a contour map, there is no excuse for not using it. All that Mr. Goss suggests that we do with a perspective drawing and a supplementary set of distribution curves or tables can be done stereographically.

In order to simplify the interpretation, all we have to remember is that a stereographic projection is just a map of the surface of a sphere. The stereographic projection has been used by cartographers. It sometimes is used in our geographies and atlases, and it would be used more frequently if distances between points on the surface of the sphere were not distorted considerably in the projection.

We are not among those X-ray analysts who are "always endeavoring to convince the metal-working industries of the importance and value of this method." We think the X-ray diffraction and the stereographic pole-figure methods are being used almost as much as they need be. The pole-figure method should not be used unless the data are very complete, and seldom in industry do we stop to collect complete data. If we were trying to "sell" pole figures, we would replot our data to represent the orientations of the cubic axes (losing reliability by inserting an interpretation between the data and its representation). Such a map, showing the directions of the ordinary cube edges, would be understood by everyone. But we have preferred to present the data as we found them, so that the reader may analyze them in his own way.

In connection with the comments in our paper on Mr. Goss's work on recrystallization textures, we have said simply that we did not observe some of the things he has reported. We made no effort to recrystallize steel cold-rolled various amounts, nor under various conditions as to time and temperature. Our work was not intended to be a complete study of the effect of all these factors.

As to his interpretation of this duplex recrystallization texture as a twin relationship, we have said simply that our pole figures are not consistent with this hypothesis. We have not been able to take half the pole-figure data and get the rest by performing the twinning operation. Professor McKeehan, I believe, has explained how rotation of  $60^\circ$  about a  $\{111\}$  direction will accomplish the same orientation change as the shearing deformation parallel to a  $\{112\}$  plane. The latter is probably the actual mechanism; the former is a convenient way to accomplish the same change in orientation.

We did not use the product of a commercial mill in our hot-rolling studies because we wanted to know the rolling temperature. Fig. 6 is typical of  $\frac{1}{4}$ -in. sheet bar. Fig. 5 may suggest that the  $\{211\}$  and  $\{100\}$  planes lie in the surface, but the texture can not be determined from one photogram.

We thank Mr. Goss for putting us right about the interpretation of his brief comments on hot-rolled rods. We understood that the photogram he showed was obtained in any direction perpendicular to the direction of rolling.

Dr. Van Horn has pointed out several of the variables in rolling which should be studied in connection with the effects we have reported; let us hope that someone will find time to do it. In answer to Mr. Hobrock, we are afraid that even an approximation of the temperature reached is beyond our powers with the available data.

## Preferred Orientations in Iron-silicon Alloys

By C. S. BARRETT,\* MEMBER A.I.M.E., G. ANSEL,† JUNIOR MEMBER, AND R. F. MEHL,‡ MEMBER

(New York Meeting, February, 1937)

It has been observed that deformation in iron takes place by slip on  $\{110\} + \{112\} + \{123\}$  planes<sup>1,2</sup>, but in silicon ferrite with low deformation temperatures or high silicon contents (exceeding 4 per cent) the authors have found that slip is confined wholly to  $\{110\}$  planes, at least with small amounts of deformation. The purpose of the present investigation was to determine the effect of this alteration of slip mechanism on preferred orientations in cold-rolled and recrystallized strips. Incidental observations on the effect of the recrystallization temperature were also made.

The numerous determinations of the texture of cold-rolled iron and steel have been in satisfactory agreement as to the principal features of the texture (with the exception of a few conclusions that apparently have been based on insufficient data). The texture is chiefly one in which  $[110]$  directions of the grains lie along the direction of rolling, with a deviation of a few degrees, and in which the  $(100)$  planes lie in the plane of the rolled sheet, with a deviation from this position chiefly about the rolling direction as an axis<sup>3-9</sup>.

This deviation about the rolling direction as an axis has been measured by different observers and lies between about  $45^\circ$  and  $50^\circ$  or  $60^\circ$  for iron<sup>5,6,9</sup> and is usually in the neighborhood of  $50^\circ$  for mild steel<sup>6,7,8</sup>. The range of this deviation is a function of the percentage of total reduction<sup>8,10</sup>. Post<sup>8</sup> reported that it decreases with increasing percentage reduction, but apparently he studied only the surface material, which Gensamer and Mehl<sup>7</sup> found to be somewhat differently oriented from the material in the inside of the sheet. McLachlan and Davey<sup>10</sup> found that the deviation also decreases with increasing percentage of total reduction for the material in the interior of the sheet and is independent of the percentage of reduction per pass.

The deviation about the cross direction as an axis (the direction in the

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‡ Director of Metals Research Laboratory and head of the Department of Metallurgy, Carnegie Institute of Technology.

<sup>1</sup>References are at the end of the paper.

plane of rolling 90° to the rolling direction) varies<sup>5-10</sup> under different conditions from about 20° to 6°, decreases with increasing percentage reduction<sup>8,10</sup> and in the surface layers decreases with increasing roll diameter<sup>8</sup>.

Exact comparisons between the results of different observers are meaningless, for the crystallites decrease in number with increasing deviation from the ideal orientation<sup>10,11</sup>, and the limit that is observed depends greatly upon the X-ray technique; e.g., length of exposure, use of white or characteristic radiation, reflection of the beam from the surface or transmission through the sheet, and grain size of the material.

In addition to the principal orientations discussed above, there are other less prominent orientations that have been described in terms of

TABLE 1.—*Summary of Recrystallization Textures*

Material	Recrystallization Temperature	Recrystallization Texture		Investigator	Method
		Rolling Plane	Rolling Direction		
Iron.....	Above 600° C.	(100)	~15° from [011]	Glocker <sup>12</sup>	X-ray
Electrolytic iron and mild steel	550° to 840° C.	(100)	~15° from [011]	Kurdjumow and Sachs <sup>8</sup>	X-ray, pole figure
		(111)	[112]		
		(112)	~15° from [110]		
Mild steel.....	650° C.	Similar to Kurdjumow and Sachs <sup>8</sup>		Gensamer and Lustman <sup>14</sup>	X-ray, pole figure
	580° C.				
		Slightly different from K. and S. <sup>8</sup>			
3.05 per cent Si.....	1100° C. <sup>a</sup>	(100)	[001]	Sixtus <sup>12</sup>	Optical, (etch pits)
		(110)	[001]		
		(110)	[001]		
3.5 per cent Si.....	1093° C. <sup>a</sup>	(110)	[001]	Bozorth <sup>11</sup>	X-ray
2.07 per cent Si.....	580° C.	Similar to K. and S. <sup>8</sup>		Present research	X-ray, pole figure
4.61 per cent Si.....	590° C.	Similar to K. and S. <sup>8</sup>		Present research	
4.61 per cent Si.....	860° C. }	Slightly different from K. and S. <sup>8</sup> and from Gensamer and Lustman <sup>14</sup>		Present research	
4.61 per cent Si.....	1093° C. }			Present research	

<sup>a</sup> With intermediate anneal (see N. P. Goss<sup>17</sup>).

ideal orientations<sup>8</sup> but that appear more consistent with the point of view<sup>5</sup> that the rolling texture is a superposition of a tension texture (the tension axis along the direction of rolling) upon a compression texture (the compression axis normal to the sheet).

The addition of nickel does not alter the preferred orientations in rolled sheets within the ferrite range of compositions<sup>10</sup>. This affords no information on the subject under discussion, however, for the effect of nickel on the slip mechanism of ferrite is unknown.

The effect of the addition of silicon has not been reported in detail, though Sixtus<sup>12</sup> has stated that with 3.05 per cent silicon, 0.05 per cent carbon the structure is one with [100] at 45° to the rolling direction (which



would be consistent with the principal orientation in iron). This composition is within the range in which the normal slip mechanism of iron operates and does not give information on the point in question.

The preferred orientations found in cold-rolled material after recrystallization seem to depend greatly upon the details of the processing treatment, though some divergence in the results of different investigators may be ascribed to differences in methods of determining the textures. The results that have been reported for iron and alloyed ferrite are summarized in Table 1. None of the silicon compositions previously reported have been sufficiently high to provide the altered slip mechanism and thus to show its effect on the recrystallization texture.

### EXPERIMENTAL TECHNIQUE

*Preparation of Alloys.*—The alloys used in this investigation were prepared by the Allegheny Steel Co. Care was taken to produce specimens as nearly identical as possible except for the silicon content, with one composition in the range where  $\{110\} + \{112\} + \{123\}$  slip occurs at the rolling temperature, and another composition in the range where only  $\{110\}$  slip occurs. The compositions were as follows:

	C	Mn	P	S	Si
Low silicon.....	0.066	0.19	0.017	0.021	2.07
High silicon.....	0.068	0.19	0.019	0.019	4.61

A 12-lb. ingot of each heat was forged to a bar  $\frac{1}{2}$  by 4 in., then hot-rolled to 0.250 in. thickness. Specimens were then sheared into strips 2 in. wide and given further treatment as follows: A strip of low-silicon alloy was heated from one hour at 898° C. (1650° F.), slow-cooled, and then cold-rolled to 95 per cent reduction. A strip of high-silicon alloy after being heated at 898° C. was air-cooled and then cold-rolled to 95 per cent reduction. The high-silicon material had to be heated to 149° C. (300° F.) for satisfactory rolling. All cold-rolling was carried out in the same direction as the hot-rolling and without intermediate heating. The rolls were 5 in. in diameter.

*X-ray Technique.*—The specimens were ground and etched equally on both sides to a final thickness of 0.006 in., thus removing all material that might have a texture characteristic only of the surface. Pole figures were plotted from the intensity maxima on the white radiation (110) diffrac-

FIG. 1.—SILICON, 2.07 PER CENT, ROLLED 95 PER CENT, BEAM NORMAL TO SHEET.

All photograms printed with rolling direction vertical, lengthwise of page.

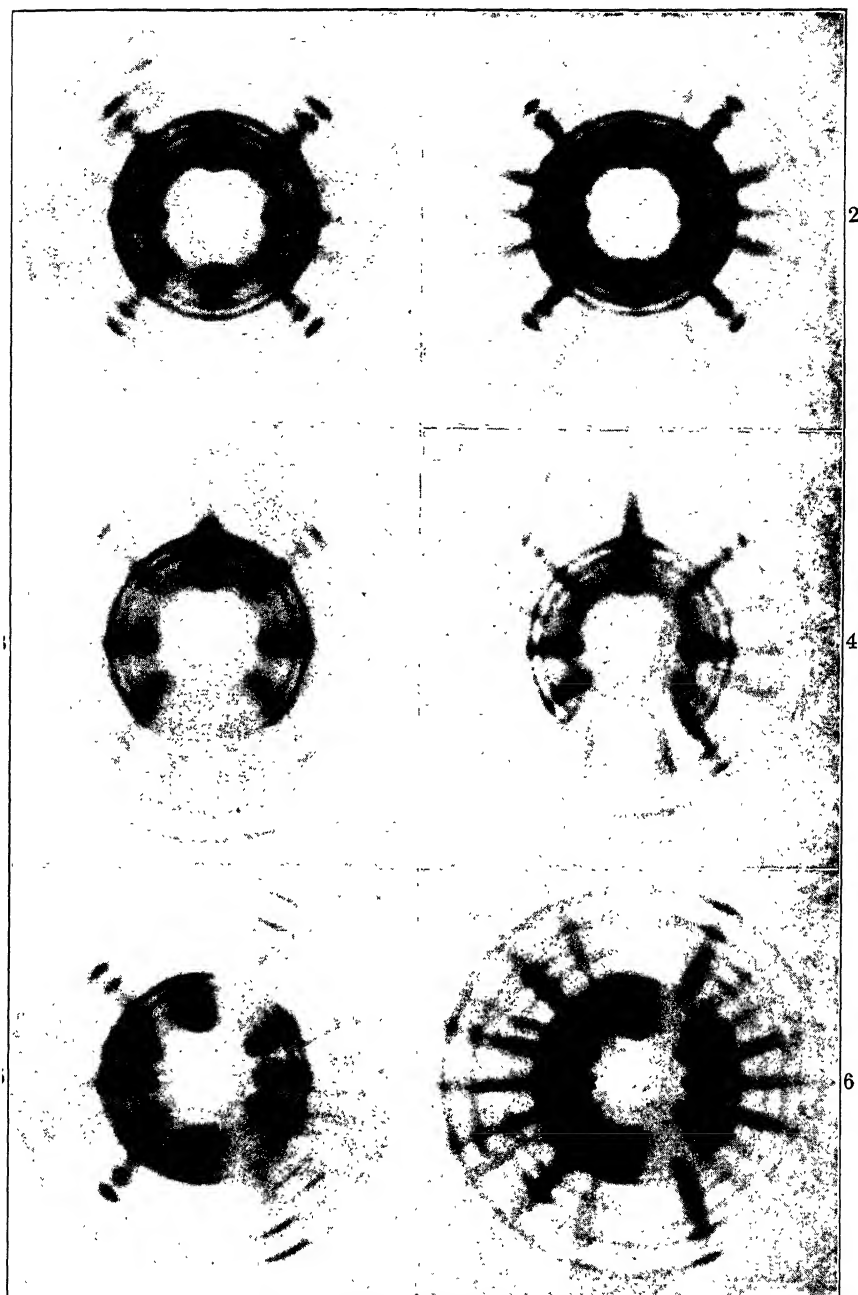
FIG. 2.—SILICON, 4.61 PER CENT, ROLLED 95 PER CENT, BEAM AS IN FIG. 1.

FIG. 3.—SILICON 2.07 PER CENT, ROLLED 95 PER CENT, BEAM 80° FROM ROLLING DIRECTION, 90° FROM CROSS DIRECTION.

FIG. 4.—SILICON 4.61 PER CENT, ROLLED 95 PER CENT, BEAM AS IN FIG. 3.

FIG. 5.—SILICON 2.07 PER CENT, ROLLED 95 PER CENT, BEAM 90° FROM ROLLING DIRECTION, 60° FROM CROSS DIRECTION.

FIG. 6.—SILICON 4.61 PER CENT, ROLLED 95 PER CENT, BEAM AS IN FIG. 5.



For descriptive legends see p. 518.

tion ring and the (200) white and  $K_{\alpha}$  diffraction rings, using a molybdenum target X-ray tube operating at 35 kv. The films were read independently by two observers and the resulting pole figures compared. Some of the recrystallized samples were of such large grain size that suitable patterns could be obtained only in a camera that provided for a shifting of the specimen parallel to itself to integrate the structure over a considerable area of the specimen.

*Confirmation of Altered Slip Mechanism.*—By the strain-anneal method a number of large grains were grown in strips of the 4.61 per cent silicon alloy (after 95 per cent cold-rolling) and were investigated for the nature of the slip lines. The strips were given a metallographic polish and deformed by reversed torsion at room temperature, the method found to be most successful in the previous investigation of slip lines<sup>2</sup>. The slip lines thus produced were those expected from the previous study: they were very straight, almost without exception, and differed in appearance from the lines in iron or low-silicon alloys. The micrographic appearance so closely resembled the characteristic appearance of {110} slip in the high-silicon alloys of the preceding study (Figs. 7, 8, 11, 12, 13 of reference 2) that there was no doubt that the 4.61 per cent silicon addition had been sufficient to alter the slip mechanism as intended.

## RESULTS AND CONCLUSIONS

*Cold-rolled Material.*—Some of the diffraction patterns of specimens with 2.07 per cent and 4.61 per cent silicon, respectively, cold-rolled to 95 per cent reduction in thickness, are shown in Figs. 1 to 6. The pole figures plotted from these photograms are reproduced in Figs. 7, 8 and 9. It will be seen from the patterns and the pole figures that the main features of the preferred orientations are identical in the two compositions. The only difference that much exceeds the experimental error is the difference in scatter about the rolling direction as an axis from the position in which [110] is parallel to the rolling direction and (100) lies in the rolling plane. The alloy of lower silicon content shows a scatter of 40° or 45° in each direction as contrasted with a scatter of 55° to 60° for the higher silicon alloy. The scatter about the cross direction is almost identical, but probably slightly greater in the low-silicon alloy. The pole figures show the same features as those for electrolytic iron<sup>6</sup> and mild steel<sup>7</sup>, a strong component corresponding to the ideal (incomplete) tension texture and a weak component corresponding to the ideal compression texture. These ideal textures are indicated in the pole figures by dot-and-dash lines.

It might be concluded from these results that the slip plane is unimportant in determining the deformation texture and that the slip direction, which most probably is unchanged by the addition of silicon, determines the texture. This conclusion is by no means certain, however, for after severe deformation the low-silicon and high-silicon alloys may have the

same slip mechanism. A second objection to this conclusion lies in the fact that in both low-silicon and high-silicon alloys the number of possible

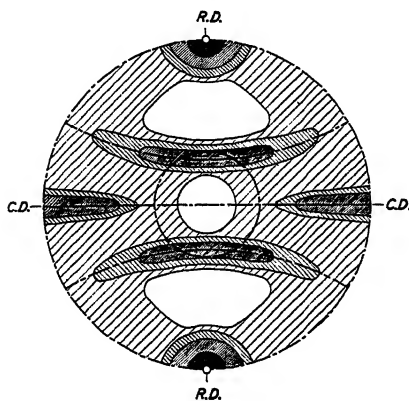


FIG. 7.

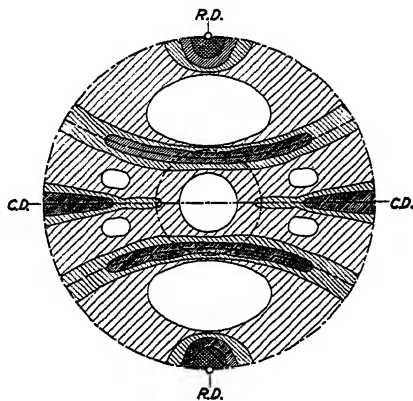


FIG. 8.

FIG. 7.— $\{110\}$  POLE FIGURE FOR 2.07 PER CENT SI ALLOY COLD-ROLLED 95 PER CENT.

All pole figures give ideal tension and compression textures as dot and dash lines. (White radiation.)

FIG. 8.— $\{110\}$  POLE FIGURE FOR 4.61 PER CENT SI ALLOY COLD-ROLLED 95 PER CENT. (WHITE RADIATION.)

slip systems is great, and the operation of one set out of this number may not differ much from another in its effect on the lattice.

*Progressive Development of the Texture.*—A search was made for a possible difference in the rate or manner of development of the final stable orientation, by making a series of exposures of strips rolled to reductions of 60 to 75 per cent. The rolling of both high-silicon and low-silicon strips was done on the same mill used before, and the same technique was used in preparing and X-raying the specimens. After hot-rolling to 0.232 in. they were held for 2 hr. at 815° C. (1500° F.), then cold-rolled to 0.093 and 0.058 in., respectively, for the samples reduced 60 and 75 per cent. The high-silicon material rolled with difficulty, the edges and surfaces of the strip showing numerous cracks and laminations. The patterns from these samples were spotty, owing to the large size of the grains before cold-rolling, but they permitted qualitative conclusions on the questions at hand.

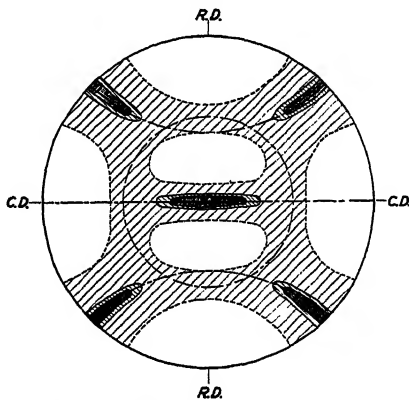


FIG. 9.— $\{200\}$  POLE FIGURE FOR 4.61 PER CENT SI ALLOY COLD-ROLLED 95 PER CENT.

Low-intensity region from  $K_{\alpha}$  radiation; high-intensity regions from white radiation.

The two alloys did not differ much either in their rates of development of the final texture or in the range of scatter in the texture. In both low-silicon and high-silicon strips the fraction of crystals having the final orientation increased with the degree of rolling, and the range of scatter

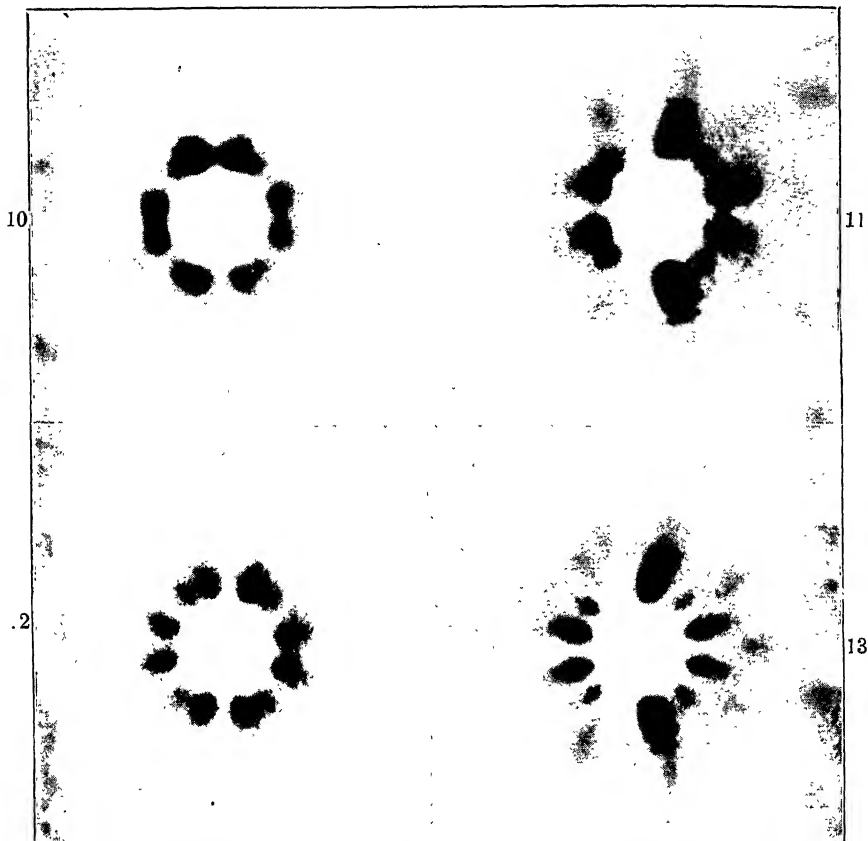


FIG. 10.—SILICON 2.07 PER CENT, ROLLED 95 PER CENT, RECRYSTALLIZED AT AND BELOW  $580^{\circ}\text{C}$ ., BEAM NORMAL TO SHEET.

FIG. 11.—SAME SPECIMEN AS FIG. 10, BEAM  $90^{\circ}$  FROM ROLLING DIRECTION,  $50^{\circ}$  FROM CROSS DIRECTION.

FIG. 12.—SILICON 4.61 PER CENT, ROLLED 95 PER CENT, RECRYSTALLIZED AT AND BELOW  $590^{\circ}\text{C}$ ., BEAM NORMAL TO SHEET.

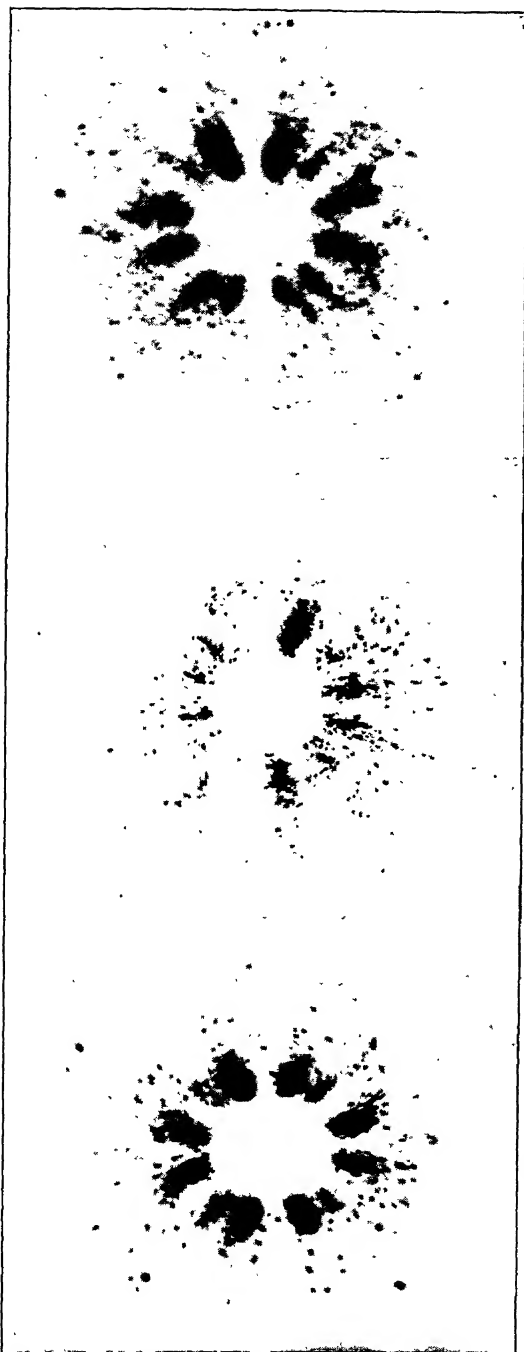
FIG. 13.—SAME SPECIMEN AS FIG. 12, BEAM  $90^{\circ}$  FROM ROLLING DIRECTION,  $50^{\circ}$  FROM CROSS DIRECTION.

around the rolling direction, if it changed at all, appeared to increase slightly rather than to decrease.

FIG. 14.—SILICON 4.61 PER CENT, ROLLED 95 PER CENT, RECRYSTALLIZED AT AND BELOW  $860^{\circ}\text{C}$ ., BEAM NORMAL TO SHEET.

FIG. 15.—SAME SPECIMEN AS FIG. 14, BEAM  $90^{\circ}$  FROM ROLLING DIRECTION,  $50^{\circ}$  FROM CROSS DIRECTION.

FIG. 16.—SILICON 4.61 PER CENT, ROLLED 95 PER CENT, RECRYSTALLIZED AT  $1093^{\circ}\text{C}$ ., BEAM NORMAL TO SHEET.



14

15

16

or descriptive legends see p. 522.

*Recrystallization Textures.*—Strips of the cold-rolled material were recrystallized at various temperatures, then prepared for X-ray examination, as before, by grinding and etching both surfaces. Specimens cold-rolled to reductions of 60 and 75 per cent had large and nonuniform grains, and produced patterns that as a rule were too spotty for the purpose of this study, but those reduced 95 per cent gave well defined patterns. As the samples reduced 60 and 75 per cent gave poor patterns that resembled in type (though less completely developed) the satisfactory ones from those reduced 95 per cent, only the experiments on the latter will be reported in detail. The recrystallization treatments for the 95 per cent material are listed in Table 2. The first two experiments in the table were designed to

TABLE 2.— <i>Recrystallization Treatments</i>	
PERCENTAGE OF SILICON	RECRYSTALLIZATION TREATMENT
2.07	100° to 580° C. in 8 hr. and cooled at same rate.
4.61	Same as above, followed by a second treatment from 100° to 590° C.
4.61	100° to 860° C. in 8 hr. and cooled at same rate.
4.61	Placed in furnace at 1093° C. for 2 min. and rapidly cooled in air.

give recrystallization at the lowest recrystallization temperature (the 4.61 per cent alloy required, in fact, a second heating to complete the recrystallization); the last experiment listed, on the other hand, was designed to cause recrystallization to occur entirely at a high temperature.

Representative diffraction patterns from these experiments are shown in Figs. 10 to 16, inclusive, and pole figures for the first three treatments are given in Figs. 17, 18 and 19. The experiment of Fig. 12 was repeated on a specimen that had been ground and etched on one side only, thus leaving one of the surface layers. The pattern was identical with Fig. 12 of the interior material. High-silicon and low-silicon alloys recrystallized below 600° C. differ but little in their texture. This indicates that recrystallization structures are not determined by the slip planes that are active at low degrees of deformation. Either they are related to the slip directions (which are presumably the same at all silicon compositions) instead of the slip planes, or the slip mechanism after severe deformation differs from the mechanism with small deformations.

The influence of temperature on the recrystallization texture is shown in the pole figure for the higher temperature treatment (heating to 860° C.) and in the patterns of Figs. 14, 15 and 16 for 860° and 1093° C. At these temperatures there are 12 definite (110) maxima on the patterns taken with the X-ray beam normal to the sheet, and the texture appears to be one of greater perfection than is produced at lower temperatures, although of the same general type. There is a possibility that the secondary recrystallization or new growth of grains noted by Wimmer and

Werthebach<sup>15</sup> in iron-silicon alloys is responsible for the difference. This growth occurs at 1000° C. with sheets reduced 20 to 30 per cent, but possibly occurs at lower temperatures with more severely worked material

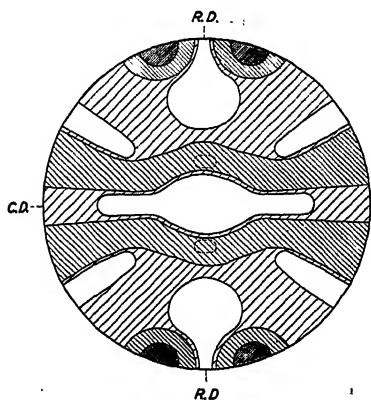


FIG. 17.

FIG. 17.—{110} POLE FIGURE FOR 2.07 PER CENT SI ALLOY COLD-ROLLED 95 PER CENT AND RECRYSTALLIZED AT AND BELOW 580° C.

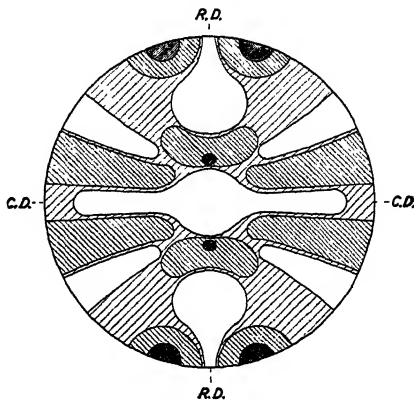


FIG. 18.

FIG. 18.—{110} POLE FIGURE FOR 4.61 PER CENT SI ALLOY COLD-ROLLED 95 PER CENT AND RECRYSTALLIZED AT AND BELOW 590° C.

such as was used here. Their investigation did not include reductions over 30 per cent.

The recrystallization textures obtained can be described as the result of rotating the rolled texture 17° each way about the normal to the sheet, or can be described equally well as the result of rotating the rolled texture 20° each way about the directions lying 35° from the normal to the sheet and 90° from the cross direction. The axes of rotation in the latter case coincide with [112] directions of a crystal in the ideal orientation. The pole figures are not greatly different from those published for electrolytic iron<sup>6</sup> and mild steel<sup>6,7</sup>, which have been described also in terms of rotations of the deformation texture (by  $\pm 15^\circ$ ) about the normal to the plane of the sheet.

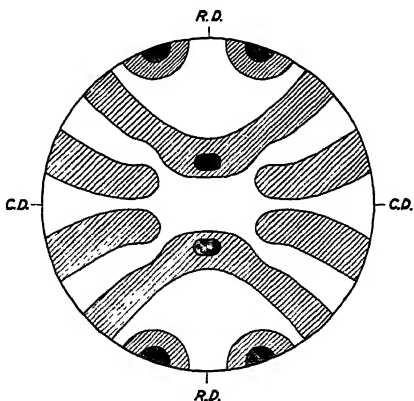


FIG. 19.—{110} POLE FIGURE FOR 4.61 PER CENT SI ALLOY COLD-ROLLED 95 PER CENT AND RECRYSTALLIZED AT AND BELOW 860° C.

The meaning of this relation is obscure. The fact that the [112] directions, about which the deformation textures appears to be rotated, lie in a (110) plane and normal to possible slip directions in that plane is suggestive of Burgers'<sup>16</sup> theory of recrystallization, but this theory is neither



strictly applicable here nor does it explain these results when it is applied.\*

Pole figures for the cube planes of the recrystallized strips are important from the magnetic standpoint. These were not constructed from the films, but can easily be derived from the (200) pole figure for the cold-rolled material. If Fig. 9 is rotated  $17^\circ$  in each direction about its center the superposition of the two rotated figures will represent the principal orientations of the cubic axes in the recrystallized strips. The cubic axes will thus be found to cluster about the normal to the sheet and about two positions in the plane of the strip, approximately  $28^\circ$  and  $62^\circ$  from the rolling direction.

The recrystallization texture is different from the one found by Bozorth<sup>11</sup> in a 3.5 per cent silicon alloy prepared by Goss<sup>17</sup>, and is different from those found by Sixtus<sup>12</sup> (see Table 1) in a 3.05 per cent silicon alloy. These two investigations, however, concern material that has received an intermediate anneal during the rolling process, whereas the strips discussed in the present paper were reduced 95 per cent after the preliminary hot-rolling and annealing. Differences of treatment of this sort are known to be critical in determining the magnetic anisotropy of rolled sheet (they are the subject of patents) and must have profound effects on the recrystallization orientation, possibly through their influence on the texture or the state of strain in the individual grains just prior to recrystallization. The mechanism underlying the relation between deformation and recrystallization textures remains one of the most perplexing problems of physical metallurgy.

#### SUMMARY

1. Iron-silicon alloys of high and low silicon content, deforming, with low degrees of deformation, in the one case on  $\{110\}$  planes and in the other on  $\{110\} + \{112\} + \{123\}$  planes, but, so far as is known, deforming with the same slip directions, have practically the same preferred orientation after cold-rolling. The textures differ merely in the amount of scatter around the rolling direction as an axis. The textures resemble closely the textures previously reported for iron, mild steel and iron-nickel alloys.

2. Progressive cold-rolling to increasing reductions in thickness does not decrease the scatter in orientation around the rolling direction as an

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\* Burgers and his coworkers have found recrystallization textures formed from cold-worked single crystals that apparently are based on local curvatures of the lattice about axes in the slip planes normal to the active slip directions. In a crystal of the ideal orientation discussed here, the slip systems subjected to the greatest shear would not have their axes of local curvature in suitable positions to explain the recrystallization textures obtained, nor would a reasonable combination of these local rotations explain them. Burgers and Louwerse<sup>18</sup> have concluded that local curvature is not an important factor in polycrystalline recrystallization textures.

axis; in both high-silicon and low-silicon alloys it increases the fraction of crystals having the final orientation.

3. The addition of silicon in amounts sufficient to alter the slip mechanism does not alter the recrystallization texture of the cold-rolled strips, nor cause it to differ markedly from the textures for mild steel recrystallized at 650° C., or from iron recrystallized in the range 550° to 840° C. The type of recrystallization texture was independent of the total percentage reduction in thickness over the range investigated, 60 to 95 per cent.

4. The recrystallization orientation found in differently treated iron-silicon alloys by Bozorth<sup>11</sup> working with material prepared by Goss<sup>17</sup> and the orientations found by Sixtus<sup>12</sup> did not appear in these specimens.

5. Recrystallization at high temperatures produces a texture of slightly greater perfection than recrystallization at minimum recrystallization temperatures, but the general features of the texture are the same.

#### ACKNOWLEDGMENT

We wish to thank Dr. L. C. Hicks, of the Allegheny Steel Co., for the specimens used in this investigation. Assistance in preparing illustrations was furnished by the Works Progress Administration and the National Youth Administration.

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## DISCUSSION

(Edmund S. Davenport presiding)

G. SACHS,\* Newark, N. J.—Today the importance of such investigations as are carried out by Barrett, Ansel and Mehl is fully recognized. For example, the magnetic properties of sheets in certain iron-nickel alloys can be fully understood only on the basis of the results of such investigations. But I am sorry that there is not yet any satisfying theory of these facts as simple as the plastic deformation of cubic crystals seems to be. One important result of this paper is that we cannot conclude from experiments on single crystals as to the behavior of the crystals in a sheet. For the above case the crystals containing silicon deform differently from pure iron, whereas the sheets deform practically in an identical manner. On the other hand, we have found that in silver-gold alloys single crystals behave very similarly,<sup>18</sup> whereas the texture in gold-rich sheets (copper type) is quite different from the texture in silver-rich sheets (brass type).<sup>19</sup> Another important result of this paper is that there is not any full agreement between the results of different investigations on the same or on very similar material. At any rate this is not particularly astonishing, remembering how complicated such processes as rolling, drawing, etc., really are. The flow of material, the "strain," depends very much upon the friction conditions which are effected by the shape, size and lubricant of the tools. We therefore have tried to find a purer state of stress and strain. Indeed, the process of deep-drawing cylindrical shells from a blank supplies suitable samples in this respect;<sup>20</sup> furthermore in such a shell there are manifold stress and strain conditions at different places. From the investigations of brass shells we concluded at first that the strain and not the stress was the important factor.<sup>21</sup> For example, the compressed fibers at the periphery gave exactly the same X-ray pictures as the fibers at the bottom, pulled in two directions, regardless of their large difference in degree of deformation (namely, about 50 and 20 per cent, respectively). On the other hand, a fiber deformed in the same manner as a rolled sheet is supposed to be given a very different texture.

To my mind, therefore, the reason for the unsatisfactory knowledge of this problem is that the behavior of the crystals in sheets depends very sensitively upon the external deformation conditions. The deformation process in single crystals is also in some cases not very regular; for example, at high symmetrical positions or at higher temperatures<sup>22</sup> they show increased gliding possibilities. I would be interested to learn whether the authors have found any case in which the polycrystalline material gave an

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\* Baker & Company, Inc.

<sup>18</sup> G. Sachs und T. Weerts: *Ztsch. Physik* (1930) **62**, 473-493.

<sup>19</sup> F. v. Göler und G. Sachs: *Ztsch. Physik* (1929) **56**, 495-502.

<sup>20</sup> L. Herrmann und G. Sachs: *Metallwirtschaft* (1934) **13**, 745-752.

<sup>21</sup> G. Sachs und E. Schiebold: *Naturwiss.* (1925) **13**, 964-968.

<sup>22</sup> W. Boas und E. Schmid: *Ztsch. Physik* (1931) **71**, 703-714.

unexpected result. This is the case for iron-nickel sheets, in which the texture can be quite different, depending upon the crystal orientation in the annealed state and the degree of deformation.<sup>23</sup>

A. B. GRENINGER,\* Cambridge, Mass.—Have the authors made any plot of pole figures whereby the original deformation structure is changed by the operation of the four possible twinning positions in the cubic lattice? I think a welcome addition to the paper would be a pole-figure plot of this kind, which should give a clear picture of the possible influence of twinning on recrystallization structures.

C. S. BARRETT (written discussion).—Dr. Sachs summarizes our conclusions in a sentence that is apt to leave slightly the wrong impression; we do not conclude that the crystals in iron-silicon sheets have the same crystallographic slip planes as iron, but we do conclude that crystals in a sheet have the same slip planes as single crystals of the same composition. The final orientations obtained in the rolled sheets, however, are practically independent of composition.

As Dr. Sachs points out, there are examples of cases where deformation textures differ without a corresponding difference in the slip planes; a familiar example of this is Schmid and Wasserman's study of textures in drawn wires of different face-centered metals.<sup>24</sup> Mr. Ansel and I have recently found another example: the compression texture of 70-30 brass differs from the compression texture of copper, yet both have face-centered lattices and presumably have the same slip planes. Apparently there is no close correlation between deformation textures and the planes that operate as slip planes at low degrees of deformation.

Dr. Sachs asks whether we have found any unexpected results in the recrystallized sheets as a result of intermediate anneals. We did not investigate the effect of different intermediate annealing treatments on the final recrystallization texture, chiefly because this problem seems to be a very complex one, and it did not appear likely that the complexities would serve as a basis for an understanding of recrystallization textures. The problem has been investigated rather thoroughly in a number of industrial laboratories, I believe, and is the subject of patents.

Regarding "unexpected results" I think I should say that I do not know what would be called an unexpected result; in recrystallization structures, almost everything is unexpected. I am continuing with some experiments in the hope of finding some general rules of recrystallization behavior.

At Dr. Greninger's suggestion, we are adding a pole figure of the orientations that would be generated from the deformation texture by twinning (Fig. 20). While there are some similarities between this twinned texture and the observed recrystallization textures, they are definitely not the same. For example, there is a minimum

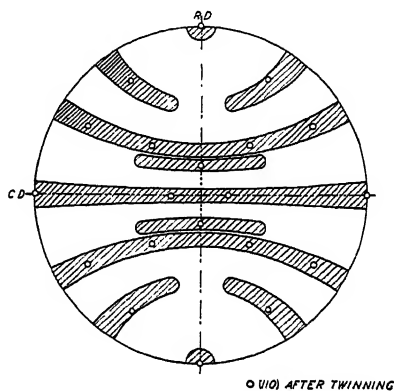


FIG. 20.—{110} POLE FIGURE FORMED BY ALL POSSIBLE TWIN ORIENTATIONS IN A GRAIN HAVING [110] PARALLEL TO THE ROLLING DIRECTION AND (100) PARALLEL TO THE ROLLING PLANE (SMALL CIRCLES).

Shaded areas indicate deviation of twinned crystals from this position, to correspond with the deviations of the rolled crystallites from the ideal position.

<sup>23</sup> O. Dahl und T. Pfaffenberger: *Metallwirtschaft* (1935) **14**, 25-28.

\* Instructor in Metallurgy, Harvard University.

<sup>24</sup> E. Schmid und G. Wasserman: *Ztsch. Physik* (1927) **42**, 779.

density of poles in the rolling direction in the observed pole figures, and a maximum in the twinned pole figure of Fig. 20. A similar disagreement occurs at the center of the pole figure. I do not see that there is any support for the twinning theory of recrystallization textures.

This same conclusion was stated in the TRANSACTIONS of the American Society for Metals (December, 1936, 24, page 1031), in a discussion on a paper by N. P. Goss. Mr. Goss did not agree, but apparently misunderstood the requirements of the twinning theory. He assumed that because the intensity maxima on his (211) diffraction rings agree with the predictions of the twinned structure, his patterns support this theory; he overlooked the fact, however, that other diffraction rings of the same films had intensity maxima which do not agree with the predictions of the twinning theory, and that all maxima must be accounted for if the theory is to be accepted.

## Oxide Films on Iron

BY ROBERT F. MEHL,\* MEMBER A.I.M.E., AND EDWARD L. McCANDLESS†

(New York Meeting, February, 1937)

### PART I. ORIENTATION RELATIONSHIPS IN OXIDE LAYERS

Oriented overgrowths and intergrowths among both metallic and nonmetallic substances have been recognized and studied for well over a century. The work of Widmanstätten in 1808 on the geometrical structure in meteorites, a structure known by his name, demonstrated that oriented intergrowths can occur in purely metallic systems. This fact led to much of the early microscopic study of alloys, contributing greatly to the advance of physical metallurgy. The problem has been attacked again in recent years in a comprehensive fashion, with the object of discovering what atomic movements may occur during phase changes in alloy systems. Much of this work has appeared in the A.I.M.E. TRANSACTIONS in a series of papers published by Mehl and coworkers beginning in 1931<sup>1</sup>. Although many aspects of this general problem remain unsolved, it may be said that the orientation of a new phase forming by precipitation from solid solution or by transformation invariably bears a unique relationship to the orientation of the phase from which it formed, and that similarity in atomic patterns on atomic planes in the two phases play an important part in determining the orientation relationship.

Analogous orientation relationships exist in oriented intergrowths in nonmetallic systems—mineral or inorganic. In 1827 Haidinger<sup>2</sup> discovered natural intergrowths of hematite and magnetite, and demonstrated that the rough form of the magnetite octahedrons was delineated by small crystals of hematite, of which the basal (00·1) planes lay parallel to the octahedral cleavage planes of the magnetite. The description of this orientation relationship was later completed by von Rath<sup>3</sup>, who showed that the edge (00·1):(10·1) in hematite lies normal to the [111]

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<sup>1</sup> References are at the end of the paper.

direction in the (111) match plane of magnetite. Similar orientation relationships have been found in more recent years for other nonmetallic systems<sup>4,5,6</sup>.

Oriented overgrowths were noted and studied as long ago as 1825<sup>7</sup>, when it was found that lead nitrate crystals occupy regular positions when deposited on alum, and also alum on boracite. This subject has been actively pursued in recent years, particularly by Royer<sup>8</sup> and by Menzies<sup>9</sup>. In this case also similarity in atomic patterns on the planes common to the two phases plays an important and probably a predominant role in determining the orientation relationships. Similar behavior has been noted in sputtered and condensed metallic films<sup>10</sup>. This latter work is of particular importance in metallurgy, for it has been shown that the lattice of the deposit adapts itself to that of the base—in aluminum sputtered on platinum this adaptation is extreme enough to alter the normal face-centered cubic lattice to a face-centered tetragonal lattice\*.

Reaction films or layers present an especially interesting case. It was proposed by Tammann<sup>11</sup> in 1922 that reaction layers, such as oxides formed directly on metal crystals by reaction with gaseous oxygen, or on silver crystals in a similar way, are oriented with respect to the metal crystal, presumably owing to some crystallographic mechanism operating during the formation of the reaction layer. The work of Elam<sup>12</sup> on the formation of  $\gamma$ -brass on  $\beta$ -brass by reaction in zinc vapor, though not sufficiently complete to furnish the full details of the reaction mechanism, at least offered qualitative support for this idea.

The formation of oxides on metals has great general interest. If it can be shown that oxides are oriented, and if the complete orientation relationships can be determined, the atomic-crystallographic mechanisms of oxidation may fairly be inferred<sup>1</sup>. Furthermore, the existence of such orientation relationships will imply the presence of atomic bonds between the oxide and the base metal; a study of these together with a study of the degree of strain induced by imperfection in lattice registry at the interface should contribute much to the study of the adhesion and stability of films on metals and thus to an understanding of the conditions under which films protective against oxidation and corrosion may form.†

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\* It is quite possible that such lattice distortions—engendered by the tendency for lattices to adapt their atomic spacings to those of neighboring lattices at interfaces—may, at least in part, account for the properties of metal crystals in the neighborhood of grain boundaries and perhaps also in a minor degree along slip lines.

† Pilling and Bedworth<sup>13</sup> showed that a metal that forms an oxide denser than the metal oxidizes at a rate that remains constant with time, for such oxide films crack during growth owing to the volume contraction, whereas a metal that forms an oxide less dense than the metal oxidizes at a rate parabolic with time, for no shrinkage cracks are formed and the metal can oxidize progressively only by diffusion of oxygen through the film, and since the amount of oxygen passing through the film must decrease with

For this purpose, the orientation relationships obtaining between the phase "FeO"\* and alpha iron, and those obtaining between the phases "FeO" and  $\text{Fe}_3\text{O}_4$  were investigated†.

### *Experimental Procedure*

Large crystals of alpha iron were prepared from hydrogen-purified Armco iron by the strain-anneal method. The simplest method of providing an oxide layer of a predetermined composition is to react iron with selected mixtures of hydrogen and water vapor at a selected temperature; any one of the phases "FeO,"  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_3$  may be obtained as an equilibrium phase by the proper selection of gas composition and of temperature‡. The pressure-temperature diagram of the  $\text{Fe-H}_2\text{-H}_2\text{O}$  shows that pure "FeO" may be formed on iron by reaction with a 50:50 mixture of hydrogen and water vapor at  $750^\circ\text{C}$ . This gaseous mixture was obtained by bubbling hydrogen through a water saturator operated in a thermostat within a temperature range of  $75^\circ$  to  $85^\circ\text{C}$ . with a control of  $0.1^\circ\text{C}$ . Four saturator towers filled with glass beads and containing water were connected in series to a hydrogen tank, with a spare tower between the saturators and the reaction tube to prevent the transport of water spray. The partial pressure of hydrogen in the resultant gaseous mixture is the difference between the partial pressure of water at a specific temperature and that of the pressure at which the whole system was operated; namely, 10 mm. of mercury greater than atmospheric. The composition of the gaseous mixture as analyzed invariably agreed with the calculated composition within 3 per cent. The equilibrium relations between iron and mixtures of hydrogen and water vapor are such that the compositions of the vapor mixtures generated in the saturation temperature range used, with allowance for variations from the calculated composition of the gaseous mixture, and for temperature fluctuations in the reaction chamber, could give the "FeO" phase only.

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the film thickness, the rate of oxidation is proportional to the reciprocal of the film thickness and the curve of weight against time is thus parabolic. (See summary given by U. R. Evans<sup>14</sup>.) Little is known, however, about the factors that determine which of the latter metals should form very highly protective oxide films, such as those on chromium and aluminum. The present study may contribute information on this point, as suggested above.

\* The phase Wüstite commonly designated as FeO does not conform in composition to this formula and is herein designated as "FeO." See reference 14.

† Preliminary announcement of the results of this work were made<sup>15,16</sup>. During the course of this work Finch and Quarrell demonstrated<sup>17</sup> that ZnO on zinc and MgO on magnesium possessed abnormal lattice symmetries owing to the requirement of lattice adaptation, and also showed orientation relationships.

‡ The most recent work on the composition of the  $\text{Fe-H}_2\text{-H}_2\text{O}$  system is that by Emmett and Schultz<sup>18</sup>.



The oxidation of the specimens was performed in a wire-wound furnace controlled automatically within  $\pm 10^\circ$  C. The gaseous mixture was transported from the saturator towers to the reaction chamber by a copper tube heated electrically to temperatures above the saturator temperature, in order to prevent condensation of water. Oxide layers considerably thicker than temper films were formed.

The "FeO" phase is not stable below  $570^\circ$  C.—it decomposes there to form  $\alpha$ -Fe and  $\text{Fe}_3\text{O}_4$ , each of which shows a solid solubility range. It was thus necessary to preserve the "FeO" phase by quenching so that its orientation could be determined at room temperature. Rapid quenching generated strains which caused the oxide film to spall or so greatly to distort that sharply defined diffraction spots could not be obtained. After many trials it was discovered that cooling of the specimen in a blast of nitrogen after moving the specimen to the cool end of the reaction tube preserved the "FeO" phase in a condition suitable for X-ray analysis.

The composition of the oxide film was confirmed by X-ray powder photograms taken with a Westgren-Bohlin camera on oxide built on iron strips in the manner described; the diffraction lines obtained agreed with those given in the literature for the "FeO" phase. The orientation of the oxide layer was determined by a stationary-oscillating camera of the Davey-Wilson type.

The orientation relationships between "FeO" and  $\text{Fe}_3\text{O}_4$  were determined by X-rays, using a layer of "FeO" formed on large natural crystals of magnetite with well developed octahedral faces by the technique described above.

The crystal structures and parameters of these various phases at room temperature are as follows: Alpha iron is body-centered cubic, with  $a_0 = 2.86 \text{ \AA}$ ; "FeO" is simple cubic of the NaCl type, with  $a_0 = 4.29 \text{ \AA}$ ;  $\text{Fe}_3\text{O}_4$  is cubic of the spinel type, with  $a_0 = 8.39 \text{ \AA}$ ;  $\text{Fe}_2\text{O}_3$  is hexagonal with parameters as given in references below.\*

### Results

X-ray photograms of the "FeO" layers on different single crystals of iron all showed the same orientation relationship, though most of the X-ray films were difficult to read because of the strained condition of the "FeO" lattice. This relationship consists in a parallelism of the cube planes in  $\alpha$ -Fe and in "FeO" that lie nearest to the plane of the surface of the specimen, and in a parallelism of the dodecahedral direction in the

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\* The sources of the diffraction data used are as follows: for FeO, Wyckoff and Crittenden<sup>19</sup>, and Hedvall<sup>20</sup>; for  $\text{Fe}_3\text{O}_4$ , Wyckoff and Crittenden<sup>19</sup>, Claassen<sup>21</sup> and Bozorth<sup>22</sup>; for  $\text{Fe}_2\text{O}_3$ , Hedvall<sup>20</sup> and Harrington<sup>23</sup>.

cube plane of  $\alpha$ -Fe with a cube direction in the cube plane of "FeO." In Miller indices we may write

$$(001)_{\text{"FeO"}} \parallel (001)_{\alpha\text{-Fe}}; [010]_{\text{"FeO"}} \parallel [110]_{\alpha\text{-Fe}}.*$$

It follows that three orientations of "FeO" can form (all, of course, with the same crystallographic relationship to the  $\alpha$ -Fe lattice) around a single crystal of iron, one for each cube plane in  $\alpha$ -Fe, for on inspection it will be seen that the "FeO" lattices formed on the three cube  $\alpha$ -Fe planes are not continuous. On a sphere (or a cylinder), therefore, it may be presumed that the orientation chosen will change at some point midway between the cube faces.

This orientation relationship suggests a very simple atomic-crystallographic mechanism for the formation of the "FeO" lattice from that of  $\alpha$ -Fe. The body-centered cubic lattice contains a face-centered tetragonal lattice with an axial ratio of  $c:a$  equal to  $1:\sqrt{2}$ , as shown in Figs. 1 and 2. If, then, at the moment of the formation of "FeO" this face-centered tetragonal lattice should expand to a face-centered cubic lattice (therefore with an axial ratio of unity) there would be formed the face-centered cubic lattice of the iron atoms in "FeO."† The selection of any of the cube axes for this expansion process will lead to "FeO" orientations differing from the first and from each other, thus producing three possible orientations of "FeO."

Thus, in atomic-crystallographic terms the process of oxidation is one in which oxygen atoms in combining with iron produce an elongation in the interatomic distances in that cube direction in alpha iron which lies nearest the direction of diffusion, in this way creating the face-centered cubic lattice of iron atoms which with the combined oxygen atoms forms the characteristic lattice of "FeO." These relationships are pictured in Figs. 1 and 2.

The similarity of the atomic arrangements on the parallel cube planes in "FeO" and  $\alpha$ -Fe respectively is shown in Figs. 3 and 4. The corresponding interatomic distances agree within 6 per cent.

"FeO" grown upon the natural octahedral faces of magnetite was found to possess an orientation relationship in which all planes of the same indices in the two lattices are parallel; i.e., the two lattices are parallel. An example of an X-ray film taken for this case is shown in Fig. 5. The plot of atomic patterns on the cube planes in these two

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\* This relationship seems to be the best that can be derived from the X-ray data. Other orientation relationships lying close to that stated might be derived from the data, but the observed parallelism of the cube planes in the two phases lying closest to the oxidation interface argues for that given.

† Inspection will readily show that the iron atoms in the simple cubic lattice of "FeO" form a face-centered cubic lattice with  $a_0$  identical with that given for the lattice of "FeO."

lattices is shown in Figs. 6 to 9, and we may again note the close similarity in atomic pattern and in interatomic distances. The atomic spacings in the two lattices differ by only 2 per cent. The patterns of iron atoms on corresponding planes are only partly similar, while those of the oxygen atoms are completely so, which is evidence in favor of Gruner's theory<sup>24</sup>

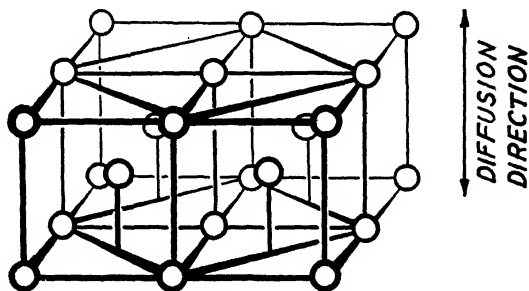


FIG. 1.—LATTICE OF BODY-CENTERED CUBIC  $\alpha$ -Fe, SHOWING FOUR UNIT CELLS WITH INTERPENETRATING FACE-CENTERED TETRAGONAL LATTICE.

that oriented overgrowths are built up with a single plane of oxygen atoms serving both lattices.

On a number of X-ray photographs of "FeO" layers formed on alpha iron, diffraction spots were observed, which were identified from their reflection angles as originating in  $\text{Fe}_3\text{O}_4$ , doubtless formed by partial

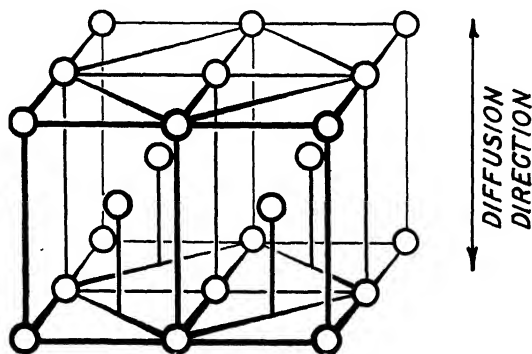


FIG. 2.—LATTICE OF "FeO" WITH THE UNIT FACE-CENTERED CUBIC CELL OF IRON ATOMS SHOWN INTERPENETRATING IN A LATTICE COMPOSED OF FOUR UNIT BODY-CENTERED TETRAGONAL CELLS OF AXIAL RATIO 1.414.

decomposition of "FeO" during cooling. Stereographic plots of the corresponding "FeO" and  $\text{Fe}_3\text{O}_4$  orientations showed that the two cubic lattices were parallel, exactly as in the reaction layer described immediately above. This observation is highly interesting because apparently

it is the first time that a fundamental similarity between overgrowths and intergrowths—Widmanstätten figures—has been demonstrated. If this

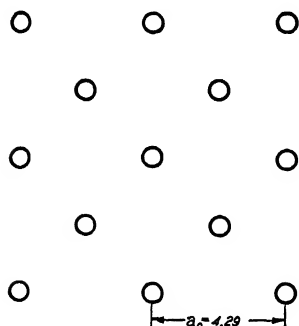


FIG. 3.—PATTERN OF IRON ATOMS ON CUBE (001) PLANE OF FOUR UNIT CELLS OF "FeO."

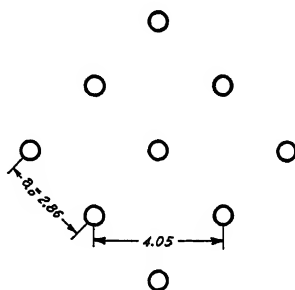


FIG. 4.—PATTERN OF IRON ATOMS ON CUBE (001) PLANE OF FOUR UNIT CELLS OF  $\alpha$ -Fe.

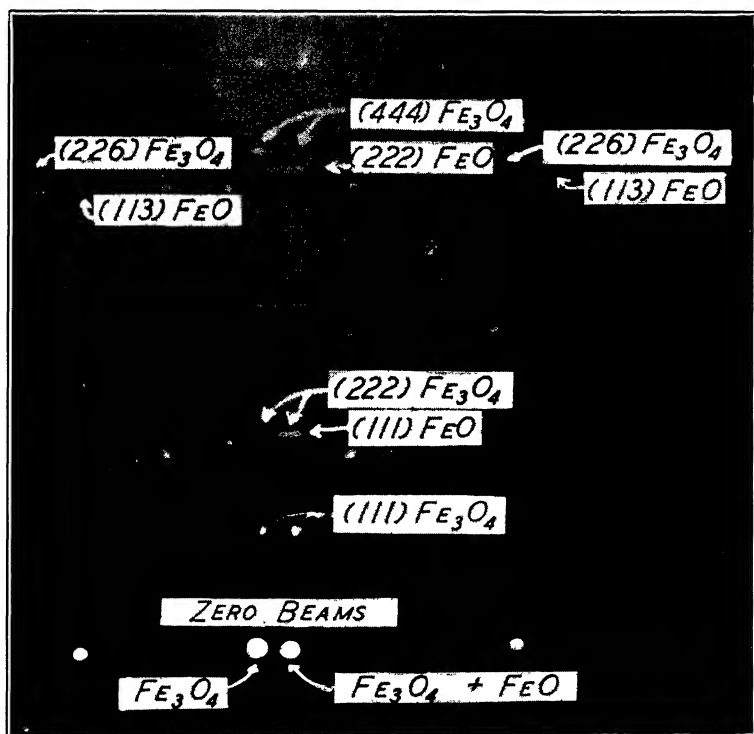


FIG. 5.—DUPLEX X-RAY PHOTOGRAPH—STATIONARY FILM IN DAVEY-WILSON METHOD—PREPARED BY SUPERIMPOSING PHOTOGRAM FOR "FeO" LAYER ON PHOTOGRAM FOR MAGNETITE BASE TAKEN IN SAME POSITION.

Identity in orientations is shown by same angular positions (when corrected for zero beam displacement) of diffraction spots of same indices.

identity in orientation relationships should prove to be general, a powerful tool will have been provided for studying the mechanism of lattice

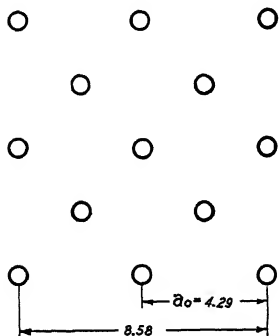


FIG. 6.—PATTERN OF IRON ATOMS ON CUBE (001) PLANE OF FOUR UNIT CELLS OF "FeO."

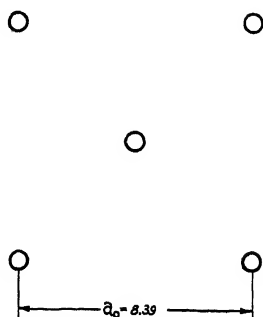


FIG. 7.—PATTERN OF IRON ATOMS ON CUBE (001) PLANE OF ONE UNIT CELL OF  $\text{Fe}_3\text{O}_4$ .

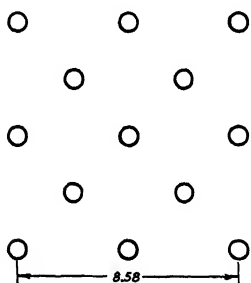


FIG. 8.—PATTERN OF OXYGEN ATOMS ON CUBE (001) PLANE OF FOUR UNIT CELLS OF "FeO."

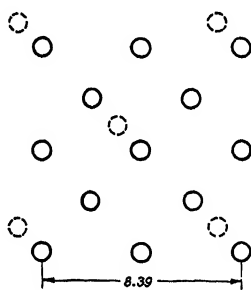


FIG. 9.—PATTERN OF OXYGEN ATOMS ON CUBE (001) PLANE OF ONE UNIT CELL OF  $\text{Fe}_3\text{O}_4$ .

Dotted circles show positions of iron atoms.

transformation, for whereas the number of systems that form Widmanstätten figures suitable for analysis is limited, the opportunities of forming reaction or diffusion layers is very great and the analysis of these relatively simple.

As stated above, many workers have observed and solved the orientation relationships in intergrowths and overgrowths in the system  $\text{Fe}_3\text{O}_4$ - $\text{Fe}_2\text{O}_3$ . Gruner<sup>24</sup> has given a plot of the oxygen atoms on the matching planes, shown in Fig. 10, which likewise show a close similarity in both the pattern and the interatomic dimensions of the oxygen atoms in the two lattices.

We see, therefore, that in the  $\alpha$ -Fe-"FeO" pair, the iron atoms show near coincidence on the interfacial plane, in the "FeO"- $\text{Fe}_3\text{O}_4$  pair there is only a partial similarity in the pattern of iron atoms but a complete one

for the oxygen atoms, and in the  $\text{Fe}_3\text{O}_4$ - $\text{Fe}_2\text{O}_3$  pair there is a complete similarity for the oxygen atoms and none for the iron atoms.

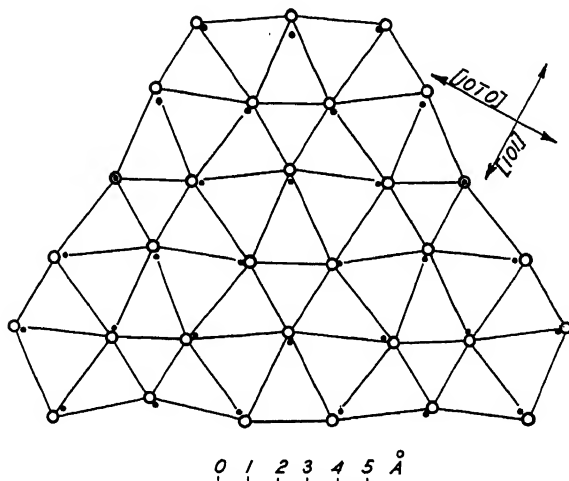


FIG. 10.—PATTERN OF OXYGEN ATOMS ON BASAL (00.1) PLANE OF  $\text{Fe}_2\text{O}_3$  (OPEN CIRCLES) SUPERIMPOSED ON PATTERN OF OXYGEN ATOMS IN (111) PLANE OF  $\text{Fe}_3\text{O}_4$  (BLACK DOTS).

No attempt was made to solve the  $\alpha$ -Fe- $\text{Fe}_3\text{O}_4$  relationship, for though  $\text{Fe}_3\text{O}_4$  can be formed alone as an equilibrium phase it is not certain that an intervening nonequilibrium diffusion layer of "FeO," however thin, might not form, thus robbing the experiment of its meaning.

## PART II. TEMPER FILMS AND RATES OF OXIDATION OF SINGLE CRYSTALS

The fact that metals oxidize at different rates on different crystal faces has been recognized for many years, and put to practical use in the heat-tinting of polished metal surfaces for microscopic examination. In explanation of this phenomenon, Tammann<sup>11</sup> suggested in 1922 that the colors are due to optical interference at the inner and outer surfaces of the oxide film, that the crystal film responsible for this interference takes its orientation from the underlying metal crystals, and that the permeability of the oxide crystals to oxygen varies with orientation as the iron crystal varies in orientation. In 1930 Tammann studied the relative rates of temper color formation on differently oriented crystals of copper and concluded that the octahedral plane tarnished more rapidly than the cube, and that the dodecahedral plane tarnished somewhat more rapidly than the octahedral, but the description of the work was too brief to be of use to other workers<sup>25</sup>.

Recently, W. H. J. Vernon<sup>26</sup> made sensitive direct-weight observations on the oxidation of iron foil, and noted some surprising phenomena.

The oxidation-time curves for oxidation at room temperature show two discontinuities, the first of which was attributed to the completion of a unit oxide lattice on the surface, and the second to the breakdown of the primary continuous film to a secondary granular film. The specimens of iron used, however, were polycrystalline and were polished only with emery, so that a detailed interpretation of the data is difficult.

The nature of very thin oxide films on metals and of the course of oxidation has interested many investigators, of whom Tammann was one of the earliest. Of the many experimental methods used, direct weight measurements and temper-color observations have been used most frequently. If the direct weight method is used the weights of film cannot be calculated in terms of thickness, owing to the lack of complete knowledge concerning the composition of the film, and concerning the state of strain and thus the density of the film. The temper-color method suffers more severe limitations, as we shall see later. The direct weight method requires specimens in foil or sheet form; that is, specimens with a very high ratio of surface area to weight, and since such material in single-crystal form is difficult if not impossible to prepare, the application of the direct weight method in the study of the oxidation of different crystal faces is not feasible.

It is important that the limitations of the temper-color or interference method be well understood. As suggested above, the chemical compositions of thin oxide films are not known with certainty. When using either the weighing or the temper-color methods, previous investigators have, for example, arbitrarily assumed that the oxide film on copper is cuprous oxide in some instances, cupric in others, and that the film responsible for temper colors on iron is the magnetic oxide  $\text{Fe}_3\text{O}_4$ . Such assumptions are difficult to justify on the basis of the constitution of the Fe-O system.

Heindlhofer and Larsen<sup>27</sup> have shown that heavy oxide scales on iron exhibit the several oxide phases " $\text{FeO}$ ,"  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_3$  represented in the Fe-O constitutional diagram at the temperature of oxidation.

Evans<sup>28</sup> succeeded in separating temper-color films from iron by anodic or iodine dissolution of the iron, and reported the presence of an opaque magnetic scale appearing below the transparent film on specimens showing two orders of temper colors, but this method of analysis may suffer from reactions between the oxide film and the solvent and from partial solution of the film.

Smith<sup>29</sup> performed similar separation experiments and found by electron diffraction studies that  $\text{Fe}_3\text{O}_4$  is the predominating oxide; however, the interpretation of electron diffraction data sometimes is still somewhat questionable.

Rates of oxidation may be evaluated either in terms of rates of increase in thickness or rates of increase in weight. The temper-color

method attempts only to measure thickness, but the uncertainty concerning the composition of the film is nevertheless very serious in calculating thickness from color.

The temper-color method computes thickness on the assumption that the colors are caused by interference between the rays of light reflected from the inner and outer surfaces of the oxide film. For a particular wave length (color), the two reflected rays will be in phase when the optical path of the one ray through the film to the metal and back to the surface again is a multiple of the wave length. For the calculation of color into terms of thickness, however, it is necessary to know the refractive index of the film; when this is not known the "equivalent air thickness" only has been given by other workers, so that such results are purely relative. Furthermore, the refractive index will vary with wave length and also quite possibly with the state of strain in the film,\* and obviously will vary also with variations in film composition.†

It will be seen that the application of the temper-color method to polycrystalline metals is beset with a special difficulty. The old observation that the different crystals in an aggregate exhibit different colors when heat-tinted is proof that the temper colors seen by the unaided eye are in reality average colors, composed of the individual colors of the individual crystallites. How far the disregard for this elementary fact vitiates published work in which thickness is computed from temper colors on polycrystalline metals cannot be said, for evidently the phenomena are extremely complicated. It may be said, however, that the study of temper films on single crystals is at least free from this objection.

One further possible source of error in determining rates of oxidation at constant temperature must be noted. Constable<sup>31</sup> showed that at temperatures of oxidation at which one complete color sequence (the full temper-color spectrum) is formed in 2 min. the surface temperatures may rise above that of the specimen by 20° C. in copper, 50° C. in nickel and 90° in iron, when the oxidation is performed in stagnant air. Since the rate of oxidation increases rapidly with temperature, this can be a serious source of misinterpretation of data; it can be avoided either by correction—which would not be easy—or by the employment of temperatures at which the rate of oxidation is so slow that no appreciable temperature rise can obtain. The latter procedure was followed in the present work.

Despite the complications that attend the use of the temper-color method for measuring the film thickness, it was thought that temper-color

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\* J. B. Nathanson<sup>30</sup> has shown that the refractive index and density of manganese in films thin enough to exhibit temper colors differ markedly from the normal values.

† Work is now underway in this laboratory on the direct determination of the refractive index of temper films.



observations on single crystals, which are of considerable interest in themselves, might at least furnish qualitative data on the effect of orientation on the rate of oxidation in single crystals; furthermore, it seemed possible that some relationship with the metal-oxide orientation relationships might be discovered. As stated in the first part of this paper, information on the factors influencing the rate of growth of oxide films on metal crystals should ultimately be of value in the study of oxidation and corrosion-resistant materials.

### *Experimental Procedure*

The material used was for the most part hydrogen-purified Armco iron strip that contained large grains as a result of the purification treatment, and for special purposes hydrogen-purified mild steel in which very large crystals had been grown by the strain-anneal technique.

The preparation of the surface was a difficult matter. The samples were alternately polished and etched slightly in order to minimize any effect that a flowed layer might exert. A cleansing program consisting of degreasing, rinsing and etching, even with many variations, was wholly unsuccessful, for it was impossible to form temper films of uniform color over the whole extent of a single crystal. The only technique of surface preparation that proved of any use was one involving a treatment of carefully polished specimens at 875° C. in hydrogen that had been highly purified with respect to water vapor and oxygen. This treatment left the specimen surface very bright, with no trace of tarnish. Individual grains could just be distinguished by means of a very slight amount of "etch glitter" left on the surface. How far the surfaces of the crystals departed from perfect planarity cannot be said, though the point may be important in this work; in this connection the experiments on cleaved crystals described below are pertinent. When the specimens were prepared as described it was an easy matter to produce temper films of remarkably uniform temper color.

The orientations of grains sufficiently large were determined by the Davey-Wilson method or by the back-reflection Laue method, whereas the orientations of small grains were determined by the etch-pit method described by Mehl and Smith<sup>32</sup>. The accuracy of this method as used here was  $\pm 5^\circ$ .

Most of the oxidation experiments were performed in 1-in. Pyrex tubes surrounded by a constant boiling liquid. The vapor was recovered through a reflex condenser; the temperature of the oxidation chamber remained constant at the various temperatures to  $\pm 0.2^\circ$  C. Ordinary air without purification was used for oxidation.

Previous workers have usually identified the temper color by mere visual observation. This method is too susceptible to individual eye

sensitivity In an effort to identify the colors more definitely, the color of each film was compared to a standard, stepped color scale, prepared by depositing layers of barium stearate on a glass surface. The colors in this color gauge also originate from phase interference from the inner and outer surfaces of the film; the gauge consisted of 13 steps, each differing from its neighbor by six layers of monomolecular barium stearate, in the sequence 11, 17, 23 . . . 83. The first layer showed a faint yellow tinge; successive steps followed the familiar color sequence throughout the first order of interference colors. The thickness of each monomolecular layer is known to be 24.0 Å. Thus it was easily possible to identify a film thickness in terms of color identity with a standard scale of thicknesses of barium stearate, a feat that any observer can readily repeat.\* All observations are reported in terms of arbitrary color numbers referred to the gauge described; thus, color 1 is that for the first step with 11 layers of barium stearate, color 2 is that for the second step with 17 layers, and so on.

### *Results and Discussion*

All the data obtained are summarized in Figs. 11 to 14. The color numbers are plotted against the square root of the time of oxidation, since it has been generally assumed that oxidation follows a parabolic law relating degree of oxidation with time, and if this is obeyed straight lines only should appear on the figures. The oxidation curves are not straight lines. The significance of this deviation is unknown: it may originate in a true deviation from the parabolic law, or it may indicate that the color of the temper films is not a true function of film thickness, owing to a complex dependence of refractive index of the films upon the thickness. It can only be said that the film with the larger color number has the greatest thickness on a given crystal, but since the orientation of the film with respect to the surface changes as the orientation of the iron crystal changes, it is not certain that comparisons of film thickness from color numbers for crystals of different orientations can be made.

Fig. 15 gives the relative oxidation rates in air at 270° C. for single crystals cut with surfaces parallel to the three principle crystallographic faces; namely, (100), (111), (110).

Figs. 11 and 12 show the rates of oxidation in air at 270° C. and 186° C. of a large number of crystal faces, the orientations of which are well distributed, as shown on the unit stereographic triangle. It was thought that such a study would disclose gradual variations in oxidation rates as crystal orientation varied gradually, but this is not so; occasionally two crystals of nearly identical orientation gave widely different oxidation

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\* The barium stearate gauge used was kindly supplied by Dr. K. B. Blodgett, of the Research Laboratory of the General Electric Co. Its preparation and properties have been described by Dr. Blodgett.<sup>23</sup>

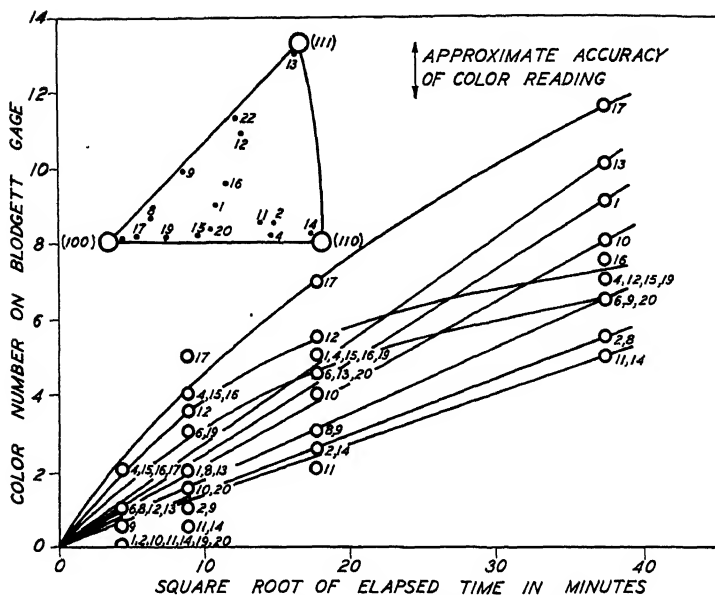


FIG. 11.—OXIDATION CURVES FOR SINGLE CRYSTALS OF IRON OF VARIOUS ORIENTATIONS, AS ILLUSTRATED IN UNIT STEREOGRAPHIC TRIANGLE. TEMPERATURE OF OXIDATION  $-270^{\circ}\text{C}$ .

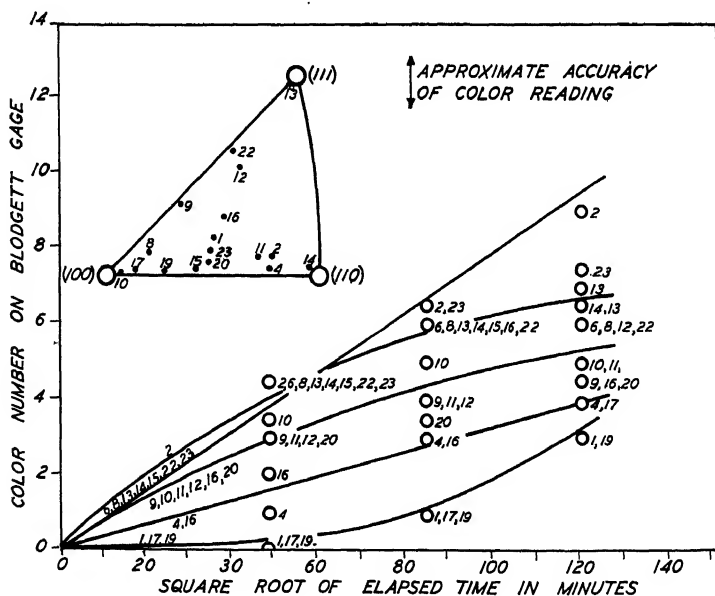


FIG. 12.—OXIDATION CURVES FOR SINGLE CRYSTALS OF IRON OF VARIOUS ORIENTATIONS, AS ILLUSTRATED IN UNIT STEREOGRAPHIC TRIANGLE. TEMPERATURE OF OXIDATION  $-186^{\circ}\text{C}$ .

rates, while crystals of widely differing orientations gave nearly identical oxidation rates. Also, the rates on two different crystals occasionally

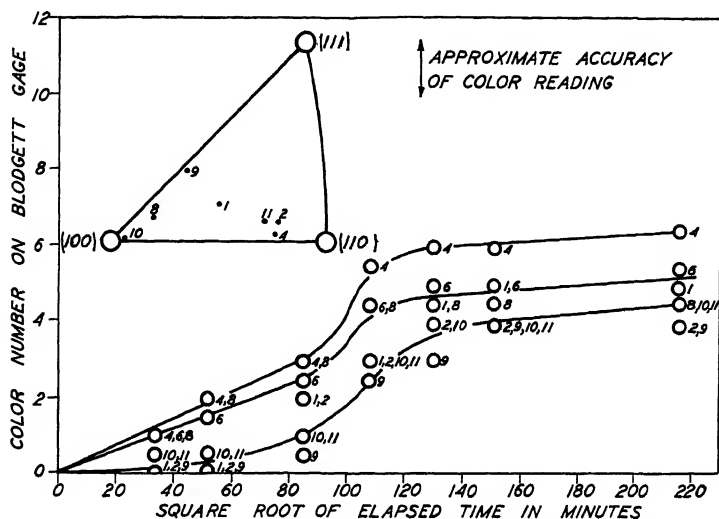


FIG. 13.—OXIDATION CURVES FOR SINGLE CRYSTALS OF IRON OF VARIOUS ORIENTATIONS, AS ILLUSTRATED IN UNIT STEREOGRAPHIC TRIANGLE. TEMPERATURE OF OXIDATION  $-140^{\circ}\text{C}$ .

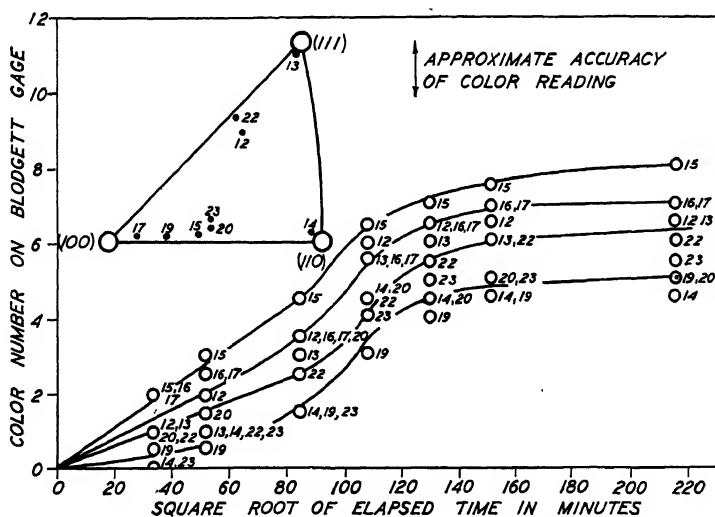


FIG. 14.—OXIDATION CURVES FOR SINGLE CRYSTALS OF IRON OF VARIOUS ORIENTATIONS, AS ILLUSTRATED IN UNIT STEREOGRAPHIC TRIANGLE. TEMPERATURE OF OXIDATION  $-140^{\circ}\text{C}$ .

invert with time; that is, a crystal that shows a faster initial rate than another crystal may show a slower final rate.

Tammann<sup>11</sup> assumed that the different heat-tint colors on crystal grains originated in different thicknesses, which in turn originated in differences in rates of diffusion of oxygen through films of different orientations. There is, however, no evidence that diffusion in cubic crystals is anisotropic<sup>34</sup>; and, indeed, calculation—as shown in the appendix to this paper—shows that there should be none. In order to eliminate any anisotropy effect originating in a thin outer layer of hexagonal  $\text{Fe}_2\text{O}_3$ , specimens of high-purity iron were oxidized to the temper-color stage by heating in an atmosphere of hydrogen and water vapor, of such composi-

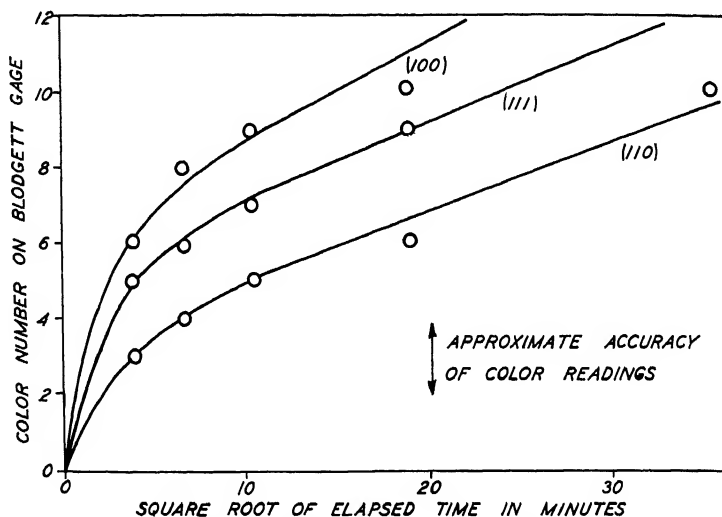


FIG. 15.—OXIDATION CURVES FOR THREE SINGLE CRYSTALS WITH THE FACES (111) (110) AND (100) EXPOSED. TEMPERATURE OF OXIDATION  $268^{\circ}\text{C}$ .

tion and at such a temperature that  $\text{Fe}_3\text{O}_4$  was the equilibrium phase and  $\text{Fe}_2\text{O}_3$  could not form<sup>18</sup>; differences in rates of oxidation on different faces were again observed, even though cubic oxide alone was formed. It is possible that different states of strain in the films on crystals of different orientations might alter the rates of diffusion, but even in this case some simple correlation with orientation should be observed which is not.

The possibility that etch pits caused by "hydrogen etching," which should show orientations on the surface varying with crystal orientation and thus give different effective or true surface areas in contrast to the apparent surface areas, lead to different rates of oxidation caused much concern. In order to study this point, large crystals were cleaved at liquid-air temperatures and the rates of temper-color formation determined in the usual manner. These cleaved crystals show little or no distortion, though slight twinning could be observed. In accordance

with much previous work, the cleavage face was found to be the cube plane (100). The oxidation curves for temper-color formation on the cleaved crystals was then compared with similar curves for the same crystal face after the crystal had been put through the usual preparation of polishing and hydrogen treatment and found to be identical within one step on the Blodgett scale, which, of course, represents the order of accuracy in these experiments.

Figs. 13 and 14 show data on the rates of oxidation at 140°. No relationship with orientation can be discovered. These two sets of curves show a mysterious change in slope at a film thickness corresponding to about the third step on the Blodgett scale; the magnitude is considerably greater than the estimated maximum experimental error. It is possible that a change in the mechanism of oxidation occurs at this thickness, perhaps fostered by an accumulation of internal stresses at the relatively low temperature.

There is nothing sporadic about the course of these oxidation curves. A given crystal repeatedly gave the same oxidation curve, within one Blodgett step, with intervening polishing and etching and hydrogen treatment. Temper films showing normal temper colors have been found in this work down to the lowest temperatures used, contrary to the findings of Vernon.

The interpretation of the rates of formation of temper films should be considered in connection with the physical state of the oxide film. It was shown in the first part of this paper that stresses in the film must result from the imperfect lattice matching in the oxide reaction layers; the resulting strain will increase as the oxide film grows thicker and ultimately should rupture the film, thus voiding any mathematical treatment of the process. The magnitude of this effect is not known, but some idea of the reality of the effect may be obtained from Fig. 16. Here it is shown that the amount of buckling of the film changes from crystal to crystal within the aggregate. The films showing the greater degree of buckling are probably the thicker films. Similar buckling phenomena have been noted on samples oxidized to a lesser extent.

Some peculiar phenomena were noted in the formation of temper films on  $\frac{3}{8}$ -in. dia. cylindrical single crystals of decarburized mild steel. These were oxidized in air at 270°. It is evident that the orientation of the surface of such a crystal will vary continuously around the crystal, with the longitudinal axis of the crystal acting as the zone axis for those planes lying parallel to the surface. The temper films on a large number of these crystals were observed not to vary gradually from point to point around the circumference of the crystal as might be expected, but to exhibit longitudinal lines along which the temper color changed abruptly, as from a deep purple to a light yellow, whereas other areas showed a

gradually varying color from point to point. These lines of sharp demarcation were invariably parallel to the longitudinal axis of the crystal. Though the orientations of these crystals were determined, no correlation with orientation could be found; the phenomenon is being studied further.

### SUMMARY

1. The orientation relationships obtaining between  $\alpha$ -iron and the phase "FeO" formed upon it by direct oxidation, and between  $\text{Fe}_3\text{O}_4$  and "FeO" formed upon it by direct reduction have been determined.

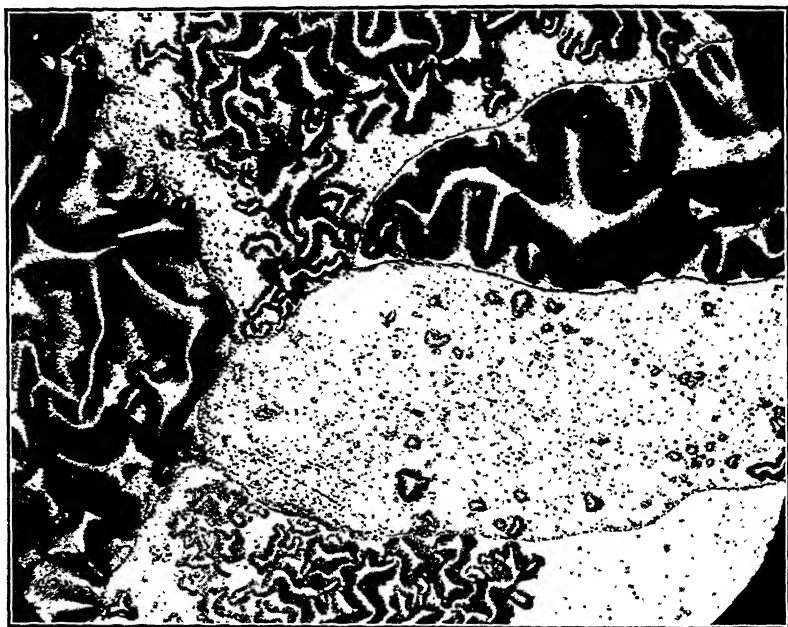


FIG. 16.—PHOTOMICROGRAPH SHOWING BUCKLING OF FILM. IRON OXIDIZED IN AIR FOR 6 HOURS AT 260° C. SIX TO TEN ORDERS OF TEMPER COLORS.  $\times 100$ .

These relationships provide a simple atomic-crystallographic picture of the mechanism of oxidation. The factors determining these orientation relationships are discussed.

2. The orientation relationships obtaining between "FeO" and  $\text{Fe}_3\text{O}_4$  formed from it by eutectoid decomposition are identical to those obtaining in oxidation layers; it is suggested that this may prove to be a general rule.

3. The limitations in the various methods for determining the rate of temper-films formation are discussed. No valid method now exists for the determination of the true thickness of films on iron in the temper-color range.

4. The rates of temper-film formation were determined at several temperatures on a large number of single crystals of hydrogen-purified iron; the thicknesses are expressed in terms of colors equivalent to those displayed by a standard gauge of barium stearate monomolecular films of known thickness. A technique of surface preparation is described which gives reproducible temper colors on oxidation.

5. Although reproducible results were obtained for crystal faces of a given orientation, no correlation of the rates with orientation could be discovered. The difference in the rates of oxidation are shown not to be dependent upon the technique of surface preparation or upon anisotropy of diffusion in the oxide layers. The rates derived are not parabolic on all crystals and show several irregularities. Micrographic evidence is given for the occurrence of severe stresses in these films.

6. A mathematical treatment is given, which shows that diffusion in cubic crystals should be isotropic.

#### ACKNOWLEDGMENT

Mr. Benjamin Lustman, a graduate student in the Department of Metallurgy at this institution, has given valuable assistance in contributing to the latter part of this experimental work.

#### APPENDIX.—MATHEMATICAL INVESTIGATION OF ANISOTROPY IN DIFFUSION IN CRYSTAL LATTICES

The occurrence of a quantity representing the interatomic distance in both the Dushman-Langmuir<sup>35</sup> and the van Liempt<sup>36,37</sup> equations for diffusion suggests that diffusing atoms move only in certain directions in cubic lattices, presumably the distance of nearest approach of atoms. The following mathematical analysis is intended to show whether or not such a mechanism of diffusion should lead to a macroscopic anisotropy of diffusion in cubic lattices.

Let us assume that the diffusion coefficient is the same for all directions in a family of directions; i.e., that in each of the six  $[110]$  directions the diffusion coefficient is the same. Let us also assume that the number of diffusing atoms is a small fraction of the whole so that interference between atoms moving along competitive directions need not be taken into consideration. We shall also assume that the diffusion coefficient is independent of concentration, though our results will not depend on this.

Fick's law states that the rate of transport of matter across any layer in a particular crystallographic direction is proportional to the normal cross-sectional area  $A_i$ , to the diffusion coefficient  $D_i$ , and to the concentration gradient  $dc/dl$  measured along that direction.



Expressed mathematically, this becomes:

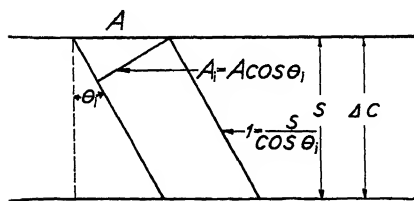


FIG. 1/.

$$\begin{aligned} \left(\frac{dW}{dt}\right)_i &= A_i \cdot D_{\{uvw\}} \cdot \left(\frac{dc}{dt}\right)_i \\ &= A \cos \theta_i \cdot D_{\{uvw\}} \cdot \frac{\Delta c}{s} \cos \theta_i \\ &= \frac{A \Delta c}{s} \cdot D_{\{uvw\}} \cdot \cos^2 \theta_i \end{aligned}$$

where the subscript  $i$  refers to directions in a particular family; e.g. [123],  $[\bar{1}\bar{2}3]$ , [231] and so forth. Summing up these expressions for all the directions in the family  $\{UVW\}$  we obtain

$$\sum_i \left(\frac{dW}{dt}\right)_i = \frac{A \Delta c}{s} \cdot D_{\{uvw\}} \cdot \sum_i \cos^2 \theta_i$$

and summing up for all possible families of crystallographic directions, we have

$$\frac{dW}{dt} = \frac{A \Delta c}{s} \cdot \sum_{uvw} (D_{\{uvw\}} \cdot \sum_i \cos^2 \theta_i)$$

The problem now is to evaluate analytically the expression covered by the second summation sign. This can best be done by adding up the expressions for the squares of the cosines of the angles between the normal to the plane of the surface of the specimen  $[uvw]$  and all the directions in the crystal of a given family  $[UVW]$ . The expression for the angle between any two directions  $[uvw]$  and  $[UVW]$  is given, for the cubic system, by

$$\cos \theta_i = \frac{uU + vV + wW}{\sqrt{\sum u^2} \cdot \sqrt{\sum U^2}}$$

We can now proceed with the addition. Since the denominator will be the same for all directions of a given family, we can sum up the numerator for a given family separately.

$\theta_1$	NUMERATOR OF $\cos^2 \theta_1$
$uvw \quad UVW$	$(uU + vV + wW)^2 = u^2U^2 + v^2V^2 + w^2W^2 + 2uvUV + 2vwVW + 2uwUW$
$UVW$	$(-uU + vV + wW)^2 = u^2U^2 + v^2V^2 + w^2W^2 - 2uvUV - 2vwVW + 2uwUW$
$UV\bar{W}$	$(uU - vV + wW)^2 = u^2U^2 + v^2V^2 + w^2W^2 - 2uvUV + 2vwVW - 2uwUW$
$U\bar{V}W$	$(uU + vV - wW)^2 = u^2U^2 + v^2V^2 + w^2W^2 + 2uvUV - 2vwVW - 2uwUW$
$UWV$	$(uU + vW + wV)^2 = u^2U^2 + v^2V^2 + w^2W^2$
$\bar{U}WV$	$(-uU + vW + wV)^2 = u^2U^2 + v^2V^2 + w^2W^2$
$U\bar{W}V$	$(uU - vW + wV)^2 = u^2U^2 + v^2V^2 + w^2W^2$
$UW\bar{V}$	$(uU + vW - wV)^2 = u^2U^2 + v^2V^2 + w^2W^2$

$$\begin{aligned} VUW & (uV + vU + wW)^2 = u^2V^2 + v^2U^2 + w^2W^2 \\ \overline{V}UW & )^2 = u^2V^2 + v^2U^2 + w^2W^2 \\ V\overline{U}W & )^2 = u^2V^2 + v^2U^2 + w^2W^2 \\ VU\overline{W} & )^2 = u^2V^2 + v^2U^2 + w^2W^2 \end{aligned}$$

$$\begin{aligned} VWU & )^2 = u^2V^2 + v^2W^2 + w^2U^2 \\ \overline{V}WU & )^2 = u^2V^2 + v^2W^2 + w^2U^2 \\ V\overline{W}U & )^2 = u^2V^2 + v^2W^2 + w^2U^2 \\ VW\overline{U} & )^2 = u^2V^2 + v^2W^2 + w^2U^2 \end{aligned}$$

$$\begin{aligned} WUV & )^2 = u^2W^2 + v^2U^2 + w^2V^2 \\ \overline{W}UV & )^2 = u^2W^2 + v^2U^2 + w^2V^2 \\ W\overline{U}V & )^2 = u^2W^2 + v^2U^2 + w^2V^2 \\ WU\overline{V} & )^2 = u^2W^2 + v^2U^2 + w^2V^2 \end{aligned}$$

$$\begin{aligned} WVU & )^2 = u^2W^2 + v^2V^2 + w^2U^2 \\ \overline{W}VU & )^2 = u^2W^2 + v^2V^2 + w^2U^2 \\ W\overline{V}U & )^2 = u^2W^2 + v^2V^2 + w^2U^2 \\ WV\overline{U} & )^2 = u^2W^2 + v^2V^2 + w^2U^2 \end{aligned}$$

$$\text{Numerator } \sum_i \cos^2 \theta_i = 8u^2U^2 + 8v^2V^2 + 8w^2W^2 + 8u^2V^2 + 8v^2U^2 + 8u^2W^2 + 8w^2U^2 + 8v^2W^2 + 8w^2V^2.$$

The denominator of  $\sum_i \cos^2 \theta_i$  is  $\sum u^2 \cdot \sum U^2$ . Multiplying this out,

we obtain

$$u^2U^2 + v^2V^2 + w^2W^2 + w^2V^2 + u^2W^2 + v^2U^2 + v^2W^2 + w^2U^2 + w^2U^2$$

which is identical with the algebraic term in the numerator. The summation thus reduces to the form

$$\frac{dW}{dt} = \frac{8A\Delta c}{s} \left( \sum_{uvw} D_{\{uvw\}} \right)$$

which is a constant, independent of  $u, v, w, U, V, W$ . If we now wish to assume from a consideration of the microscopic mechanism of diffusion that the diffusion coefficient has values  $D_{\{112\}}, D_{\{110\}}, \dots$  in the crystallographic directions  $\{112\}, \{110\}, \dots$ , we have as the equation for the transport of matter across the crystal the expression

$$\frac{dW}{dt} = \frac{8A\Delta c}{s} (D_{\{112\}} + D_{\{110\}} + \dots)$$

which is entirely independent of the orientation of the crystal  $[uvw]$ . Thus we have proved the theorem that although diffusion may be anisotropic on a microscopic scale, it must be isotropic on a macroscopic scale in the cubic system, owing to the symmetry of the cubic crystal system. The above mathematical treatment has been carried out for the hexagonal system far enough to show that all the expressions are much more complicated, and that a series of asymmetrical terms come into the equations which do not cancel out, as did the cross multiplication terms in the above.

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## DISCUSSION

(Bradley Stoughton presiding)

B. STOUGHTON,\* Bethlehem, Pa.—Any fundamental data, even the beginning of fundamental data on formation of oxide films, touch several very practical and interesting problems, among which I might mention scaling, decarburization, corrosion protection, adherent films as against films that clear off, and so on. In addition, we have here an exceedingly interesting example of the application of a new method of test of the problem.

J. B. AUSTIN,† Kearny, N. J.—I should like to ask Dr. McCandless two questions. In the oxidation of iron in an atmosphere which gives  $\text{Fe}_3\text{O}_4$  as the stable oxide phase, is a layer of  $\text{FeO}$  formed first or does the  $\text{Fe}_3\text{O}_4$  form directly on the iron? Has he made any measurements of the reflection of polarized light by these films? Tronstadt, who developed this method for films formed in water, claims that it gives an indication of both the thickness and refractive index of the film, and it would be interesting to learn what information the method yields on films formed by oxidation in air or a controlled atmosphere.

The use of Blodgett scale is very clever and the authors are to be commended for their ingenuity.

U. R. EVANS,‡ Cambridge, England (written discussion).—The authors' work promises results of fundamental value if the method of measuring film thickness can be improved. They will not, I am sure, regard it as unfriendly if certain points are indicated, which seem to require attention.

The use of temper colors as measures of thickness involves two sources of error. First, refractive index alters with wave length, and the ratio of the thickness of the oxide films to that of the reference films (whether air or barium stearate) will not be constant. Secondly, while the thickness of the film may, under favorable circumstances, fix the center of the absorption band, it does not necessarily fix the color pro-

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‡ Metallurgical Laboratories, Cambridge University.

duced. A broad absorption band and a narrow absorption band, having their centers at the same wave length, will not, in general, confer the same sensation to the eye. Thus the color sequence given by oxide films on metals (where the band may, under favorable conditions, be reasonably narrow) differs from that given by air films between glass (Newton rings colors). For instance, in the Newton rings a green occurs at the end of the first order, because the second absorption band enters the blue region of the spectrum before the first has left the red. On metals, owing to the smaller breadth of the bands, the first band leaves the visible part of the spectrum before the second band has entered it, and there is a silvery hiatus before the first and second-order colors. I have discussed these matters and the errors which they involve in several papers.<sup>38</sup>

There are two ways of overcoming these errors. One method, used sixty years ago by Wernicke<sup>39</sup> and more recently by Constable,<sup>40</sup> employs a spectroscope to find the wave length corresponding to the center of the bands, which, with the index of refraction, leads to an exact knowledge of the film thickness. The other way is to calibrate the color scale, for the films in question, by means of some more accurate method. This plan was adopted for the study of silver iodide films by Bannister and myself.<sup>41</sup> The films were measured by three quite independent methods (gravimetric, electrometric and iodometric) and the satisfactory agreement obtained between the three sets of values gave confidence in their substantial correctness. It then became possible to prepare a series of standards of thickness (silver specimens tinted to different colors) which were used in the subsequent experimental work; obviously it is better to compare one silver iodide with another silver iodide film than to compare it with an air film or a barium stearate film. In this way, time-thickness curves were plotted, showing the growth of silver iodide films under controlled conditions. The effect of several variables (temperature, stirring, concentration, nature of solvent, etc.) was explored; in each series of experiments, all the variables except one were kept constant, so as to isolate the effect of this factor. Smooth curves were obtained, obeying, in most cases, the parabolic law.

Recently, in this laboratory, Miley<sup>42</sup> has carried out a similar comparison of the thicknesses of iron oxide and copper oxide films in the interference range and found satisfactory agreement between the results of three independent methods.

The authors' work on the effect of crystalline direction upon film growth is of considerable interest. Most investigators have endeavored to avoid considering this factor by using poly crystalline material. Clearly, if the material is such that there are an infinite number of orientations distributed sporadically, the orientation variable is eliminated. With rolled foil, it may be objected that there is preferred orientation conferred by the rolling, but probably, after abrasion with emery, the structure is sufficiently confused for the purpose. A completely jumbled structure is, from the mathematical standpoint, the simplest case, and it was logical that it should be the first to receive experimental study.

Nevertheless, the time has now come to approach more difficult cases, and the work of the authors in obtaining orientation relations between film and metal is most valuable. The simplest case is the study of the rate of oxidation of important crystal faces with simple indices such as (100), (110), and (111). Fig. 15 is stated to show the rate of oxidation of these three faces, but apparently they were obtained by cutting the crystals, and it is difficult to see how this could be done without disturbing the

<sup>38</sup> U. R. Evans: *Koll. Ztsch.* (1934) **69**, 129, and earlier papers quoted therein.

<sup>39</sup> W. Wernicke: *Pogg. Ann.* (1878) **8**, 68.

<sup>40</sup> F. H. Constable: *Proc. Roy. Soc.* (1927-28) **A 117**, 376, 385.

<sup>41</sup> U. R. Evans and L. C. Bannister, *Proc. Roy. Soc.* (1929) **A 125**, 370.

<sup>42</sup> U. R. Evans and H. A. Miley: *Nature* (1937) **139**, 283.

orientation of the surface atoms. Certain planes could be produced by etching a section of polycrystalline iron so as to produce a series of facets representing a definite crystallographic direction. This might possibly overcome this particular difficulty, but it might introduce others. In Figs. 11 to 14, the authors have used surfaces which did not, except as a coincidence, correspond to any simple crystal plane; it is not very surprising that no simple correlation of the rates with the orientation could be discovered.

The procedure of cleaning with hydrogen is also likely to cause complications. Presumably hydrogen, which can diffuse readily through iron, will tend to distort the original lattice structure, and if the hydrogen reduces the original oxide film, it may leave a surface layer of spongy iron whose orientation does not necessarily correspond to that of the iron basis. It is, of course, easier to criticize the method adopted than to suggest the perfect method, but it is possible that a method of etching, under conditions where passivity can be completely avoided, would give crystal faces corresponding to a known simple crystalline direction in a state which would not need hydrogen cleaning.

I hope the authors will continue their work. If the X-ray method of obtaining orientation and crystal structures could be combined with more reliable methods of measuring film thicknesses, the results would be really valuable.

H. A. MILEY,\* Cambridge, England (written discussion).—The authors have used monocrystalline iron whereas previous studies of the iron oxides have been carried out on polycrystalline iron. This suggests that a comparative study of certain results might be valuable. What they have said concerning the composition of the oxides and the interference colors observed is of great interest.

They have described orientation relationships (a) between  $\alpha$ -iron and " $\text{FeO}$ ," and (b) between this oxide and  $\text{Fe}_3\text{O}_4$  obtained by direct oxidation or reduction under specified conditions. It seems important to consider the possibility that  $\gamma\text{-Fe}_2\text{O}_3$  is sometimes formed instead of  $\text{Fe}_3\text{O}_4$ —in which case the same orientation relationships will probably apply to the  $\gamma\text{-Fe}_2\text{O}_3$ . There is considerable evidence<sup>43</sup> that the oxide formed on polycrystalline iron when exposed to air at temperatures below  $200^\circ\text{C}$ . is  $\gamma\text{-Fe}_2\text{O}_3$ , and that the one formed above this temperature is  $\alpha\text{-Fe}_2\text{O}_3$  until  $\text{Fe}_3\text{O}_4$

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<sup>43</sup> An outline of the evidence is as follows: The oxide formed on iron in air is believed to be: (1)  $\alpha\text{-Fe}_2\text{O}_3$  when heated at temperatures above  $200^\circ\text{C}$ . (it is ferric oxide, see references below<sup>a,b,c,d,h,i</sup>; nonmagnetic<sup>a</sup>; hexagonal in structure with lattice dimensions suitable for this oxide<sup>c</sup> until an underlying layer of  $\text{Fe}_3\text{O}_4$  appears when heated at temperatures above  $400^\circ\text{C}$ .<sup>a,h,i</sup>—this possibly accounts for the  $\text{Fe}_3\text{O}_4$  found in tinted films, by Smith<sup>d</sup>, and (2)  $\gamma\text{-Fe}_2\text{O}_3$  when formed at temperatures below  $200^\circ\text{C}$ . (it is different from the oxide formed above  $200^\circ\text{C}$ .<sup>a,h,i</sup>; cubic in structure with a lattice dimension suitable for  $\gamma\text{-Fe}_2\text{O}_3$  or  $\text{Fe}_3\text{O}_4$ .<sup>c,e,i</sup>; ferric oxide<sup>a,f,g,h,i</sup>). The references used in this outline of the evidence are:

<sup>a</sup> U. R. Evans: *J. Chem. Soc.* (1927) 1020; (1930) 478.

<sup>b</sup> U. R. Evans and J. Stockdale: *Jnl. Chem. Soc.* (1929) 2651.

<sup>c</sup> W. H. J. Vernon: *Trans. Faraday Soc.* (1935) 31, 1668.

<sup>d</sup> N. Smith: *Jnl. Amer. Chem. Soc.* (1936) 58, 173.

<sup>e</sup> H. R. Nelson: *Nature* (1937) 139, 30 (did not mention  $\gamma\text{-Fe}_2\text{O}_3$ ).

<sup>f</sup> I. Iitaka, S. Miyake and T. Iimori: *Nature* (1937) 139, 156.

<sup>g</sup> U. R. Evans and H. A. Miley: *Nature* (1937) 139, 283.

<sup>h</sup> H. A. Miley: Carnegie Scholarship *Mem.*, 25.

<sup>i</sup> H. A. Miley: Unpublished work.

begins to appear as an underlying layer at temperatures well above 400°. According to this view, the oxide produced by the authors at 140° and 186° might have been  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and that at 268° and 270° might have been  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, unless the *monocrystalline* iron forms different oxides from polycrystalline iron.

Vernon<sup>44</sup> noted that films obtained by heating *polycrystalline* iron in air at temperatures below 200° gave no bright colors, even when the thicknesses were greater than required for such interference effects; this has been confirmed by Miley.<sup>45</sup> The authors report interference colors on *monocrystalline* iron when heated at temperatures below 200° as well as when heated at higher temperatures. It is known that Fe<sub>3</sub>O<sub>4</sub> has a low transparency and since  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> is so nearly the same in structure, it might be expected to have a low transparency also. The close similarity between the positions of the iron atoms in the iron lattice and the lattice of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, or Fe<sub>3</sub>O<sub>4</sub>, might cause a relatively poor reflecting plane to be produced at the metal oxide interface. Evans<sup>46</sup> has analyzed the production of interference colors by oxide films and found that it depends largely on (1) the reflection at the back of the film, (2) the transparency of the film, and (3) its uniformity. He pictures the light (of interference wave length) within the film, as being reflected back and forth between the two surfaces until it is completely absorbed or emerges *in phase* with the light reflected from the outside surface. If the reflection at the metal oxide plane and the transparency of the film are imperfect, the light will have lost part of its intensity before it emerges from the interior of the film, and the wave lengths nearest to the interference value will be reflected back and forth the greatest number of times, before they can emerge in phase, and will therefore suffer the greatest loss in intensity. If the intensity of the emerging light is plotted against the wave length, an absorption band is obtained with a minimum value at the interference wave length. Obviously, the width of the absorption band, which depends on the three factors named above, may vary from an *infinitely narrow* one to a *very broad* one; either of these will give no colors, whereas colors of different brightnesses will be given by bands between these limits, and the bands of intermediate widths will be most favorable to the production of colors.

An explanation of the differences observed in the interference effects produced by oxide films is now possible. The  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (hexagonal structure) on polycrystalline iron is possibly crystallographically discontinuous with the metal base and affords a good inner reflecting plane and it is known to have a relatively high transparency. It will therefore give an absorption band that is medium to broad. Constable's optical measurements<sup>47</sup> of the bands for these films appear to be broad. The same film on *monocrystalline* iron would have all of the optical conditions repeated except it would provide a smoother and better inner reflecting plane and be more uniform, and these differences would tend to shift the band from medium toward the narrow. Thus an  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> film on either polycrystalline or *monocrystalline* iron would be expected to give colors. The  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> or Fe<sub>3</sub>O<sub>4</sub> (cubical structure) on polycrystalline iron is possibly in optical continuity with the metal base and provides a poor inner reflecting plane and has a low transparency, and will give an absorption band that is too broad to produce colors. The same film when formed on *monocrystalline* iron will have a smoother inner reflecting plane, in addition to forming a more uniform film, and will therefore give a band that is *not* too broad for colors. No metal can be expected to produce a film so nearly perfect in uniformity, transparency and reflection that the

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<sup>44</sup> W. H. J. Vernon: *Trans. Faraday Soc.* (1935) **31**, 1674.

<sup>45</sup> H. A. Miley: *Carnegie Scholarship Memoirs*, **25**.

<sup>46</sup> U. R. Evans: *Chem. Ind. Rev.*, **4**, 211; at the foot of page 212, the figures " $\lambda/2$ ,  $3\lambda/2$ ,  $5\lambda/2$  . . ." should read " $\lambda/4$ ,  $3\lambda/4$ ,  $5\lambda/4$  . . .," as pointed out by U. R. Evans, *Koll. Ztsch.* (1934) **69**, 129.

<sup>47</sup> F. H. Constable: *Proc. Roy Soc.* (1927-28) **A117**, 381, 382.

absorption band will be too narrow to give colors, as has been realized with a collodion film discussed by Evans.

W. H. J. VERNON,\* Teddington, England (written discussion).—The authors say (p. 547): "temper films showing normal temper colors have been found in this work down to the lowest temperatures used, contrary to the findings of Vernon." Inasmuch as the authors' observations refer to films on *single crystals of massive metal* whereas I was concerned with films on a *polycrystalline surface of thin sheet*, this statement is would hardly seem to be justified. The findings to which the authors refer, being statements of experimental fact, cannot be contrary to other experimental facts obtained under other conditions; nevertheless, the divergence between the two groups of results clearly calls for interpretation.

In their computations of film thicknesses the authors rely on data calculated from the respective "temper colors," but they very rightly point out the weaknesses of this method. These weaknesses militate seriously against the use of the method to decide whether oxidation follows a parabolic course with time; such information can be obtained only by strictly quantitative observations as yielded, for example, by the gravimetric method, which shows that for the polycrystalline surface a parabolic relationship is followed very closely above a critical temperature of approximately 200°, below which there is a very considerable defection (ref. 26, p. 1675). Nevertheless, in Figs. 11, 12 and 15 (186° to 270° C.) the authors' curves at all events show an oxidation that is increasing progressively with time, as would be expected. On the other hand, in Figs. 13 and 14 (140° C.) the curves become parallel to the time axis. If the curves really represented rate of growth this would clearly mean that the film ceases to thicken within the period of the experiment. This is certainly not true for the polycrystalline material, and there seems to be no reason why it should be true for a single crystal. More probably it means simply that a stage is reached when the *color remains constant while the growth of film continues*. This is in harmony with the conclusion reached in the course of my work, namely that below the critical temperature in the neighborhood of 200° C. the film has a granular structure. On this view, the colors observed on single crystals below the critical temperature are diffraction colors, the particular color being a function of grain size and not of film thickness.

A further important corollary follows. If the film on a single crystal below 200° assumes a constant color (as distinct from a color which develops progressively through the spectrum and starts over again as must be postulated for films above the critical temperature), and, furthermore, if the precise color reached varies sporadically from crystal to crystal, then it is clear that under such conditions a polycrystalline surface should exhibit either no definite color, or colors over a very much narrower range. This is in accordance with experimental observation, because, at the lower temperatures (even at the higher limits) the only color observed is a pale brown or straw yellow, though the thickness may be such as would correspond to a deep blue above 200°; more prolonged heating merely results in a general darkening, with no further color development.

Fig. 12 (186°) calls for comment because these curves fall into the category of Figs. 11 and 15 and not Figs. 13 and 14 as would be expected if the transition temperature were exactly 200°. Actually, it was not possible in my work to determine the critical point with great precision, although it certainly appeared to be slightly below, rather than above 200°; moreover, its precise location may well depend upon the material used, and in that case some difference would naturally be expected in results obtained from large-crystal, massive material on the one hand and polycrystalline thin sheet on the other.

The authors' "hydrogen etching" at 875° is of great interest, but for the guidance of other workers in this field it would also be of interest to know just what was the

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method of etching (presumably by immersion in acid) which they abandoned in favor of the more elaborate process. The authors are much to be congratulated upon this paper, which marks a definite advance in our knowledge of oxidation phenomena.

E. L. McCANDLESS AND R. F. MEHL (written discussion).—As Dr. Austin suggests, it would be interesting to know whether or not an intermediate layer of "FeO" is formed when a crystal of iron is oxidized in an atmosphere in which at the temperature used  $\text{Fe}_3\text{O}_4$  alone is stable. Of course, such a layer would not be an equilibrium phase, but as long as any iron is left, as long as the sample is not single-phase, the possibility of nonequilibrium phases cannot be excluded; above  $570^\circ$  such an intermediate layer would beyond question be formed, and even below  $570^\circ$ —at temperatures where "FeO" has no true stability—it might well form as a transitory, perhaps very thin layer. Probably only an electron diffraction determination of lattice structure types in the neighborhood of the iron: oxide interface could furnish a satisfactory answer.

No attempt was made to use Tronstadt's polarized light method for examining the oxide films. Such a method is open to one of the same objections as in any other optical method, namely, that when a multiple-layer film is studied it is most difficult to determine to which layer or combination of layers the experimental data apply.

Comment by Dr. Evans on the subject of films is always to be especially welcomed. It has been evident for some years, as Dr. Evans remarks, that a more accurate method of calibrating film colors in terms of actual thickness is badly needed. While we, as others who have worked in this field in recent years, have been quite aware of the elementary physics involved in the formation of temper colors, we have attempted to proceed with the present studies with the best means available; the Blodgett scale provides a better means than mere visual observation of colors which has been employed by so many workers, for it can be readily reproduced; the careful matching of film colors to the steps on the scale thus provides at least a closer identification of comparable colors if not of film thicknesses. Our own attempts to use the spectroscope to determine the wave length corresponding to the center of the absorption band, though undertaken with enthusiasm, were ultimately abandoned in disappointment; the lack of data on refractive indices on composite films of such extreme thinness and the uncertain variation of this with orientation militate against the success of the method. However, even if the observed colors could be calculated accurately to true thicknesses, these thicknesses could not or could only approximately be calculated to weight increments owing to the uncertain density of the material composing the films. The very recent success of Dr. Evans and Dr. Miley in obtaining good agreement among gravimetric, electrometric, and iodometric measurements of temper film thicknesses is certainly to be welcomed.

Thus, though the method of temper-color identification is admittedly of uncertain value in appraising film thicknesses, it seemed likely that it is of somewhat less uncertainty in comparing film thicknesses; since the disregard by previous workers of orientation effects, and in general of the crystallographic properties of films has left a lamentable gap in our knowledge of films, it seemed desirable to adopt the comparison method and to attempt to evaluate the possible effects of orientation on the rate of growth of films. Needless to say, these comments do not apply to the first section of the paper in which the orientation relationships alone are described.

We distrust methods intended to avoid orientation effects by the use of polycrystalline samples with randomly oriented grains: films grown on such samples will be a composite of films of colors varying from grain to grain since the rates of color generation on grains of different orientation differ widely, and thus the orientation effect is not avoided and the color is not simple but composite. Nor could abrasion be relied upon utterly to destroy preferred orientations—abrasion itself can generate

such orientations. Thus in our opinion the simplest procedure and by far the most logical procedure is to determine rates of oxidation on the different crystal faces, and from these data to proceed to the more complicated case of aggregates with a more or less random orientation of the individual grains; this logic alone has sufficed to clarify the many difficult points in the closely analogous case of the plastic deformation of metals.

There can be no doubt that cutting the crystals produced a disturbance, but apart from cleaving no other method of producing plane surfaces was available. The technique of heating in hydrogen, however, we believe to be somewhat better than Dr. Evans suggests: the crystals, still intact, were of a single sharply defined orientation, identical with that of the base crystal with which the surface was integral.

The difficulty concerning etch pits is a serious one. Etching in aqueous solutions—this particularly in answer to Dr. Vernon's question—consisted for the most part in acid attack, both by immersion and by swabbing. The samples were first treated with a number of cleaning solutions designed to remove dirt, particularly grease; many acids in many concentrations were tried, with and without applied electrolytic potential, but in no case could uniform oxidation temper colors be developed over the whole surface of a single crystal, whereas this became a very easy task after hydrogen treatment. The occurrence of etch pits on the surface of the hydrogen-treated crystals might well have been a seriously disturbing characteristic; we believe, however, that the identical rates of color development on a cleaved crystal and a hydrogen-treated cut crystal, described on pages 546 and 547, argue powerfully against the seriousness of the part which etch pits play in the phenomena observed, though the circumstance would have been happier if the comparison were not limited to a single type of crystal plane. In passing it should be noted that the lack of exact coincidence of the crystal plane on the surface of the oxidized sample with planes of low indices could not possibly have caused us to fail to discover a simple correlation between rates of oxidation and orientation; with rates varying in a simple fashion with orientation, these rates should show a continuous variation over the extent of a unit stereographic triangle, which could be expressed as contour lines of some oxidation rate constant, much as elastic moduli or yield points of single crystals have been represented in variation with orientation.

Dr. Miley's remarks are very interesting indeed, and valuable, but we believe call for no reply. He kindly wrote us some months ago about his own work and about the results we have presented here.

We were particularly glad to have Dr. Vernon's instructive discussion. We are sure that there will be no confusion concerning the results on the rates of oxidation of single crystals of iron and of polycrystalline iron, which Dr. Vernon seems to fear, for the text is clear enough on the point. We have enjoyed Dr. Vernon's philosophical discourse on the matter; we had stated previously (page 540) that his observations had been made on polycrystalline iron and this was implied in the sentence quoted. It would be very interesting to see whether polycrystalline iron foil, the surface of which had been prepared by the hydrogen-treatment method, would give the same results as in Dr. Vernon's experiments; the difference in the modes of surface preparation constitutes another difference between our work and that of Dr. Vernon.

## Fine-grained Structural Steels for Low-temperature Pressure-vessel Service

By A. B. KINZEL,\* WALTER CRAFTS† AND JOHN J. EGAN,† MEMBERS A.I.M.E.

(New York Meeting, February, 1937)

THE demands of the petroleum and chemical industries for steels to be used in pressure vessels and similar structures at artificially low temperatures are continually increasing, and the writing of proper specifications with suitable tests becomes increasingly important. Likewise, the selection of suitable steels for such applications is of increasing concern to the metallurgist. It is generally recognized that highly alloyed steels of the austenitic stainless type retain their properties even at very low temperatures and represent the best technological solution of the low-temperature steel problem. However, in many instances less expensive carbon or low-alloy steels suitable for service within limited temperature ranges are available. The problem thus becomes one of defining the various factors involved in the production and fabrication of these less expensive steels and determining the temperature ranges in which their properties justify engineering application. Most of the applications involve welded structures, and the heat effect of welding as well as the nature of the weld metal are matters of prime concern.

The first problem that the metallurgist faces is the determination of the type of test to be used as a criterion of the performance of the steel in low-temperature service. It has been generally recognized that the static properties of steel as determined in the ordinary tensile test undergo a gradual and relatively slight change as the temperature of test is lowered in the range of current interest; i.e., from room temperature to minus 120° C. It is further generally recognized that the behavior of steel under impact involving notch sensitivity is definitely affected at the lower temperatures. While the major subject of this paper is the effect of grain-refining deoxidizers, of low-alloy additions and of welding on the low-temperature notched-bar impact properties, an inquiry into the general behavior of steel under low-temperature impact testing is included. This is a pertinent portion of the investigation and the results thereof are

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necessary to an interpretation and understanding of the data presented in the major study.

Much work has been done on the subject of low-temperature impact testing in the past few years. A great deal of this has been devoted to the effect of alloying elements, but comparatively little attention has been given to the effect of grain-refining deoxidizers. Most investigators have recognized that the method of manufacture plays an important role. Herty and his co-workers<sup>1</sup> showed the beneficial effect of aluminum used as a grain-refining deoxidizer on the low-temperature properties of plain carbon steels. Fry<sup>2</sup> investigated the improvement in the physical properties as a function of the type of deoxidation, and Sykes<sup>3</sup> and Hopkins<sup>4</sup> demonstrated the effect of grain size on the low-temperature properties of steels for welded structures. The present paper includes a more detailed study of the effect of deoxidation on the low-temperature impact strength of steel suitable for certain structures used in the as-rolled, normalized, or stress-relieved conditions. It further includes a study of the function of moderate chromium-copper alloy additions in connection with such deoxidation. The work shows definitely that the shock resistance at low temperatures is greatly increased by most of the grain-refining deoxidizers used both in the plain carbon and low-alloy steels. It further shows the effect of low-alloy additions in maintaining the low-temperature impact strength as the mass in question is increased. The role of such deoxidizing and alloying additions in inhibiting the reduction of impact strength on material next to the weld as a result of the welding operation is likewise investigated. The results indicate that welded pressure vessels and similar structures can be produced for safe operation at temperatures as low as minus 120° C. using low-alloy steels suitably deoxidized.

#### METHOD OF TESTING

All impact tests described in the paper were made on the standard 120 ft.-lb. capacity Izod machine, although two types of specimen are mentioned. One of these represents the standard notched Izod test piece 0.394 in. (10 mm.) square with a 45° notch 0.079 in. deep, and having a bottom radius of 0.010 in. The standard notch was milled with a fly cutter carefully ground to match a templet. When the notch was lapped, the notch was milled to slightly less than the desired depth, and was lapped to the proper depth and contour with a male die of suitable shape. In the second type, of similar cross-sectional area, a hole was drilled tangent to the center line using a No. 47 drill (0.078 in. diam.). The hole was then opened to the surface. These test pieces were also broken in the Izod machine, using a special jig to properly align the specimen.

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<sup>1</sup> References are at the end of the paper.

The test pieces were cooled to the test temperature in liquid media. Immersion for 30 min. to 1 hr. was followed by a quick transfer to the Izod vise, with the immediate release of the hammer. Stop-watch measurements showed that the complete operation was carried out in from 3 to 5 sec. Temperature loss during this interval has been shown (Yamada<sup>5</sup> and others) to be negligible. The liquid used varied with the temperature desired; viz., room temperature to minus 20° C. iced water or iced brine; from minus 20 to minus 78° C. acetone cooled with dry ice; from minus 78° to minus 120° C. propane cooled by means of liquid air. The production of temperatures from minus 78° to minus 120° C. was carried out with considerable care, the propane being placed in a Dewar flask and a copper tube containing the liquid air immersed in it until the desired temperature was reached. At no time was any difficulty found in maintaining the temperature constant within  $\pm 3^\circ$  C. Temperatures in the lower ranges were measured with a calibrated thermometer.

#### PART I. THE IMPACT TEST AND THE NATURE OF THE LOW-TEMPERATURE NOTCHED-BAR IMPACT PHENOMENA

There has been some confusion in the interpretation of impact-test data because under apparently identical conditions various steels will give widely different notched-bar impact test values in specific temperature ranges. This has been encountered by many of the investigators in the field. These investigators further report that decrease in the shock resistance with low temperature is not gradual but progresses by discontinuous, abrupt steps. Accordingly, the first portion of this program was designed to determine whether the apparently erratic results could be systematized, and whether these results were due to minor variations in the method of impact testing or to some characteristic behavior of the material under the conditions of test.

The values shown in Fig. 1 are illustrative of the results obtained from low-temperature Izod tests. These were obtained from tests on aluminum-treated S.A.E. 1020-X normalized and stress-relieved  $1\frac{1}{16}$ -in. plate in the longitudinal direction. The steel had a McQuaid-Ehn grain size of No. 8. As similar behavior has been encountered in every steel investigated, the specific composition and treatment are not significant. Fig. 1 shows that the impact values occurred in three distinct ranges. At temperatures slightly lower than room temperature, the energy absorbed in the impact test increased slightly. At minus 50° C. the first discontinuity was noted. Some of the samples broke at about 72 ft-lb. and some in the range of 25 to 45 ft-lb. As the testing temperature was further lowered to minus 78° C., the higher values disappeared completely and another group of values appeared at a very low level. The intermediate range from 25 to 45 ft-lb. was decreased slightly to 20 to 40 ft-lb., and the new range occurred in the neighborhood of 10 ft-lb. As the temperature

was further lowered to minus 120° C., values in the 20 to 40 ft-lb. bracket disappeared and those in the 10 ft-lb. bracket were moderately lowered. Owing to the spread of values in the intermediate range, it might be argued that these values are a continuation of the low range. However, the discontinuity appears so consistently and is frequently so well defined as to be indicative of a distinct difference in the mechanism of failure.

Dotted lines are used in the curve to indicate the temperature range in which values may occur in any one group. Similarly, the average curve indicates the proportion of breaks that may be expected to fall in each energy range. To establish this point further, four identical specimens, which were less than standard size in order to not exceed the capacity of the machine, were placed in the vise and tested at a temperature at which values in two energy levels were obtained on specimens

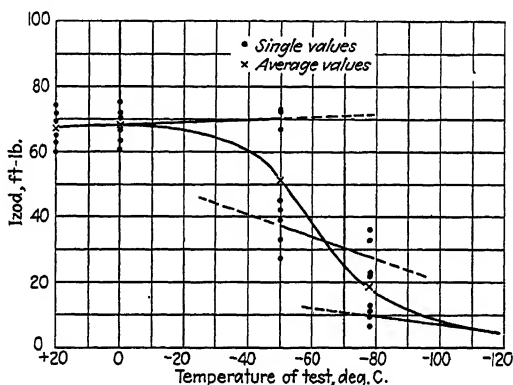


FIG. 1.—TYPICAL VARIATION OF IMPACT STRENGTH AT LOW TEMPERATURES.

broken singly. All four specimens were then broken by a single blow. Some specimens broke with a brittle fracture and some with a tough fracture. When the value obtained on brittle specimens broken singly multiplied by the number of specimens showing a brittle type of fracture, and the value obtained on tough specimens broken singly multiplied by the number of specimens with a tough fracture, were added together, the sum was equal to the energy found when several specimens were broken simultaneously. This indicates that an average value based on a sufficient number of specimens is a reliable index of the notched-bar impact properties of the steel. However, the average should be accompanied by information on the value of the energy levels involved, or at least the minimum value obtained.

It has been suggested that minor variations of factors involved in the method of testing may be the major cause for the apparent discontinuous behavior of the material in the low-temperature notched-bar impact test. Accordingly, test specimens were taken from a rolled 1½ in. plate normalized at 900° C. and drawn at 625° C. for one hour in the original

section, the steel showing medium grain size and having the following analysis: carbon, 0.10 per cent; manganese, 0.68; silicon, 0.21; copper, 0.58; nickel, 0.63; chromium, 0.77. One set of specimens was prepared using the standard V-notch with a radius of 0.01 in. and machined with the standard fly cutter, this cutter being matched to a templet. Another set of specimens was prepared with a V-notch cut in the same way and then carefully lapped. A third set was prepared with a V-notch cut as in the first case but a special bottom stop for aligning the specimens was used. A fourth set was prepared with the keyhole type of notch for use in the Izod machine. Specimens were broken, with the results shown

TABLE 1.—*Effect of Type of Notch on Low-temperature Izod Impact Strength of Chromium-copper-nickel Steel*

Description of Test	Impact Strength, Ft-lb.		
	At +20° C.	At -78° C.	At -100° C.
V-notch, fly cutter.....	94.0	61.5	31.0
	95.0	66.0	44.0
	96.0	69.0	49.0
	96.0	73.0	58.0
	96.5	76.5	61.0
	101.0	102.0	69.0
Average.....	96.4	74.7	52.0
V-notch, lapped.....	91.5	61.5	8.5
	92.0	64.0	47.0
	92.5	79.5	53.5
	93.0	102.5	54.5
	93.0	104.5	61.0
	94.0	105.5	73.0
Average.....	92.7	86.3	49.5
V-notch, special jig.....	92.0	78.5	8.0
	94.5	92.0	16.0
	96.0	103.5	43.0
	98.0	104.5	53.0
	97.5	105.5	65.0
	98.0	105.9	67.5
Average.....	96.0	98.3	42.1
Keyhole notch.....	36.0	38.0	29.0
	37.0	42.0	29.5
	38.0	42.0	31.0
	38.0	44.5	40.0
	39.5	46.6	41.0
	39.5	49.0	41.0
Average.....	38.0	43.7	35.3

in Table 1. At room temperature, the greater consistency of the values with the lapped V-notch is apparent, and the values are very slightly lower than with the unlapped notch. This difference is of a minor order, and the spread in the values of the specimens with the unlapped notch is not sufficient for concern. The higher average value at minus 78° C. indicates some effect due to the elimination of secondary notch effects by the lapping operation, but again the difference is not of a major order. This effect would be given more weight were it not for the series of results obtained at minus 100° C., in which the average values are practically the same in both series with a single low value in each case, the lapped specimen giving the lowest value. The discontinuous energy levels at approximately 95, 65 and 30 ft-lb. are apparent in both series of specimens. These results show that the mechanical preparation of the notch proper is a minor factor with minor effect on the energy values, and cannot be considered to account for the occurrence of values at widely different energy levels.

The effect of the jig used to align the specimens in the impact vise was investigated with the thought that the heat transfer through the jig produced a local increase in temperature in the notch. This temperature change, variable from specimen to specimen, might be a minor factor having a major import. Accordingly, a special bottom stop was used that did not require the use of a knife edge to align the specimen, and the same series of tests was performed at plus 20°, minus 78° and minus 100° C. Again the values fell in the previously determined energy ranges and again there was very little difference in the order of magnitude of the average results or ratio of number of values in a given range at a given temperature. Small local temperature changes, therefore, appear to have only a minor effect on the final energy values.

That variation in the actual temperature from specimen to specimen may account for the difference in the energy values obtained from various specimens should be considered. However, the values, split into two or more energy levels, occur over too wide a temperature range for such an explanation to be tenable, and the work on the columbium-treated steel, later reported, is further and conclusive evidence on this point.

To investigate further the effect of the notch, specimens of the same steel were prepared using the standard Charpy keyhole notch, and the specimens were then tested in the 120 ft-lb. Izod machine. The lower values obtained in this case at room temperature were probably due to the smaller amount of material behind the notch. The results were quite consistent, and it is significant that values at minus 78° C. fell in a single energy range. This is consistent with the reduced sensitivity to be expected with this type of notch as compared to the V-notch. However, at the lower temperature of minus 100° C., values at two energy levels were again obtained, showing that even with this type of notch, the



notch sensitivity is sufficient to bring about the same type of reaction in the material as with the sharper notch.

In order to determine whether the firmness with which specimens were held in the vise was significant, other series of tests were performed in which a more rigid vise was used, and in which the specimens were held more tightly than usual in some instances and more loosely than usual in others. Again, the discontinuous drop in impact strength at the lower temperatures and the splitting of energy values into two or three ranges were noted. Moreover, room-temperature test results under these conditions were consistent even when the tests were performed on relatively brittle material. All of this indicates that the discontinuous variations in energy absorption are not a function of minor factors in the preparation of the notch or in the testing procedure. The results also indicate that gross sharpness of the notch may alter the temperature at which the levels appear and the amount of absorbed energy of the different levels. Factors such as mass and velocity have not been investigated to more than a very limited extent, and also appear to produce quantitative differences in the locations of the discontinuous energy levels but do not eliminate these different levels. However, as factors such as the gross sharpness of notch do materially modify the discontinuous phenomena, there is a strong implication that different energy levels are produced by a combination of factors that may be implied in the term "notch sensitivity."

This is further borne out by an additional series of tests in which specimens of 0.5 per cent chromium, 0.5 per cent copper medium-grained steel were tested at minus 100° C. One series of specimens was prepared from normalized and stress-relieved material, the notching of the specimen being performed after the heat-treatment. The other series was notched prior to heat-treatment, and it should be noted that specimens of both of the series were heat-treated in the standard Izod specimen section. The specimens notched after heat-treatment in the usual manner gave values approximating 5 ft-lb. at minus 100° C., whereas those heat-treated after notching gave consistent values in excess of 100 ft-lb. at minus 100° C. Notches in specimens heat-treated after notching were then re-cut to an increased depth of 0.015 in., the re-cutting being performed after the heat-treatment, and the results of tests at minus 100° C. again gave values of the order of 5 ft-lb.

Carbon-steel specimens were then tested in a similar manner. The energy values resulting from tests at room temperature were increased slightly by notching before heat-treatment, but the values obtained at minus 100° C. were less than 2 ft-lb. in all cases, a marked contrast to the behavior of the chromium-copper steel. It is obvious, therefore, that some factor other than the proportions or smoothness of the notch has played a major role. Possible factors are cold-work produced by the

notching tool, residual stresses due to notching, oxidation and decarburization, as well as crystal orientation. To check this matter further, specimens were normalized before notching and then stress-relieved at 650° C. after notching. In all specimens, including the chromium-copper steel, the values at minus 100° C. were low, indicating that cold-working and residual stresses were not major factors in the improved impact strength of the finally normalized chromium-copper steels. Again, a series of tests on specimens normalized with the notch filled with refractory cement, to keep oxidation at a minimum, resulted in values of over 100 ft.-lb. at minus 100° C. in the chromium-copper steels. Microscopic examination revealed no decarburization. Similar tests on plain carbon steel showed that 0.20 per cent carbon boiler plate showed no appreciable

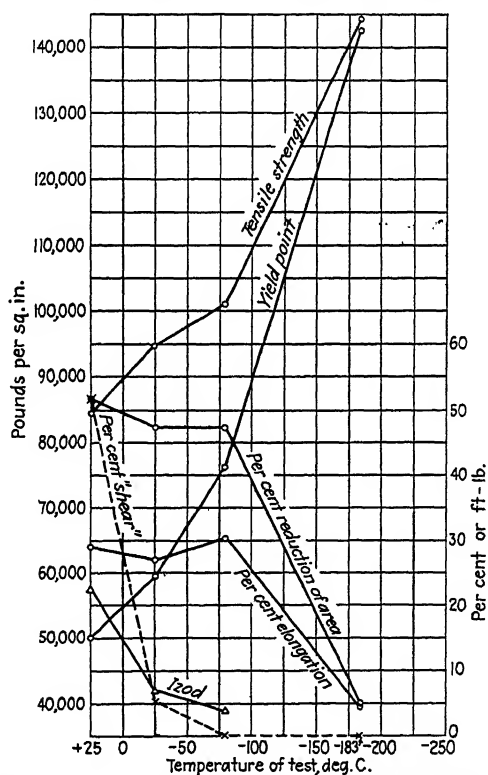


FIG. 2.—TENSILE AND IMPACT PROPERTIES OF S.A.E. 1035 STEEL AT LOW TEMPERATURES.

difference in low-temperature impact results whether the notch was cut before or after normalizing. Two ft.-lb. at minus 100° C. resulted in either case. Again S.A.E. 1020-X aluminum treated and normalized in the 0.394-in. section before notching gave 89 ft.-lb., and normalized after notching with the notch protected by refractory cement gave

84 ft.-lb., a difference of no significance. These results point to crystal orientation or some as yet unknown factor as predominant in influencing the sensitivity of the notch.

The various series of tests reported in the foregoing pages are all definite in character, but each tends to a negative conclusion. However, taken as a whole the results indicate strongly that the character of the metal at the base of the notch is of prime importance, and that the discontinuous values of energy absorption in impact at low temperatures reflect a property of the metal immediately behind the notch. Perhaps this is just another way of saying that the notch sensitivity of the material under the mass-velocity relationships involved in the usual notched-bar impact test is critical.

With the thought that it is indeed strange that the properties having such a marked effect in the notched-bar impact test appear to be in nowise reflected in the ordinary tensile test, this matter was once more investigated. Specimens of a normalized S.A.E. 1035 steel were sub-

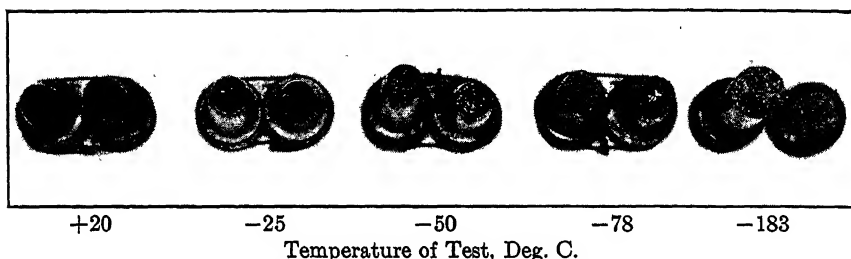


FIG. 3.—FRACTURES OF TENSILE SPECIMENS OF S.A.E. 1035 STEEL.

jected to the standard Izod test as well as to the standard 0.505-in. dia. tensile test at low temperatures. The shift in the energy values to a lower range in the impact test occurred at about minus 25° C., and the tensile properties as measured showed no discontinuity in this range. These results are shown in Fig. 2. In spite of this lack of discontinuous change in tensile properties, however, a startling change in the character of the fracture was noted (Fig. 3). At room temperature, the usual cup and cone fracture took place on static testing, with approximately 50 per cent of the area failing in shear and 50 per cent as a break across the specimen, commonly termed "tensile" or "cleavage" failure. At minus 25° C., however, only 5 per cent of the fracture of the tensile specimen showed the shear type of failure and 95 per cent of the fracture showed tensile failure. At still lower temperatures, tensile failure predominated to a still greater degree, and at minus 183° C. shear failure even as skin effect was completely absent. This definitely shows that a different mechanism of failure is involved at the lower temperatures in the static test, even though it is not indicated by an abrupt change in the strength and ductility as usually measured. It is not surprising that this different

mechanism of failure should be reflected in different energy levels in the notched-bar impact test.

It is appreciated that the above series of experiments failed to result in a positive conclusion with respect to the mechanism of failure of material under notched-bar impact conditions or under static conditions at low temperatures. The work has, however, shown that the phenomenon in question is directly associated with the steel proper rather than with the method of testing. The reality of the energy levels found in impact testing has been established, as has the fact that at certain temperatures values from apparently identical samples will fall into one or the other of the energy levels. The factors that cause a given sample to fall into a higher or lower range remain undetermined, and while several plausible hypotheses might be proposed, the advancement of hypotheses not subject to proof would not seem to be particularly constructive.

The accurate evaluation of the notched-bar impact performance of materials at low temperatures seems to necessitate the use of a sufficient number of samples to obtain values at each energy level. The ratio of the number of high and low energy values may then be determined and an average value calculated. With the present state of the art this average value would seem to be a suitable index of the sensitivity of the material to notched-bar impact failure at the temperature in question, although the value of the lower energy level is important as the limiting value. These average values and limiting values have been used, where available, as a criterion throughout the subsequent work on the effect of the deoxidizers, the effect of the alloying elements, and the effect of welding. When the number of values is small, where averages were not considered reliable, individual values have been given.

## PART II. EFFECT OF DEOXIDIZERS

### *Comparative Effects of Aluminum, Zirconium, Vanadium, Titanium and Columbium*

Although various tests have been reported on the impact strength of steels treated with aluminum, vanadium and zirconium, very few of these have been made under conditions that allow quantitative evaluation of the results. Accordingly, a series of tests was performed on steels produced under controlled conditions in the laboratory. These deoxidizers, as well as columbium and titanium, were added to the low-carbon chromium-copper steel in amounts sufficient to give a McQuaid-Ehn grain size of No. 6 to 8 or finer. Base composition, content of special deoxidizer and resultant properties are shown in Table 2, the impact tests being performed at room temperature, minus 78 and minus 100° C. on specimens machined from forged and normalized 1-in. dia. bars.

Confirming our earlier work<sup>4</sup>, the chromium-copper steel without a special deoxidizer gave relatively high values throughout, and it is signifi-

cant that each of the deoxidizers, with the exception of titanium, further improved the energy absorption on impact testing at the low temperatures. The energy values of the lower carbon aluminum-treated material are particularly interesting, in that little loss of energy absorption took place down to minus 100° C. In the higher carbon steel, aluminum tended to retain the energy values at low temperature to a lesser degree than in the lower carbon ranges. Vanadium, zirconium and columbium each resulted in a retention of increased proportions of room-temperature

TABLE 2.—*Low-temperature Izod Impact Strength of Chrome-copper Steels Treated with Various Deoxidizers*

Composition, Per Cent				Deoxi- dizer, Per Cent	Tensile Strength, Lb. per Sq. In.	Impact Strength, Ft.-lb.					
C	Cr	Cu	Si			At +20° C.		At -78° C.		At -100° C.	
							Average		Average		Average
0.15	0.73	0.45	0.21	None	76,000	78.0 77.8	77.9	51.8 47.6	49.7	43.2 32.2	37.7
0.14	0.76	0.62	0.22	0.07 Al	72,000	82.2 83.0	82.6	91.0 84.8	87.9	89.0 84.8	86.9
0.25	1.04	0.50	0.27	0.10 Al	85,000	57.2 57.0	57.1	27.0 43.0	35.0	30.0 18.4	24.2
0.16	0.78	0.60	0.17	0.12 V	85,000	47.6 66.0	56.8	43.0 34.0	38.5	31.0 49.9	40.5
0.13	0.71	0.60	0.19	0.05 Zr	70,000	75.5 75.0	75.3	78.0 83.2	80.6	65.5 32.0	48.8
0.16	0.73	0.49	0.25	0.16 Cb	70,000	75.0 75.2	75.1	81.0 53.0	67.0	30.0 51.6	40.8
0.17	0.77	0.63	0.33	0.11 Ti	78,000	73.0 73.1	73.1	13.8 6.0	9.9	5.5 18.5	12.0

impact values at the lower temperature. The effect is somewhat involved with the increased tensile strength and proportionately lower room-temperature impact values. The result of this increased tensile strength is well illustrated by the 0.25 per cent carbon aluminum-treated steel, and here again the retention of impact strength at low temperature is ample for engineering purposes.

Little more need be said as to the effect of vanadium and zirconium, as the role of these materials has been generally recognized. While vanadium improves the shock resistance, it also raises the tensile strength so that the net result is a series of impact values comparable with those of the higher carbon aluminum-treated steels. Zirconium increases the

low-temperature impact strength without any secondary effects, and may be considered in the same category as aluminum from this standpoint. The definitely deleterious effect of titanium additions is surprising, particularly in contrast with the effect of the other deoxidizing elements with which it is usually classed.

TABLE 3.—*Izod Impact Values on Columbium-treated Steels*

Mark	Composition, Per Cent						Impact Strength, Ft.-lb.								
	C	Mn	Si	Cr	Cu	Cb	Room Temperature		-78° C.			-100° C.			
									Average		Average		Average		
3976	0.21	0.44		Nil	Nil	Nil	52.0	59.8	55.9	4.0	4.2	4.1	3.0	1.0	2.0
3988	0.18	0.51		Nil	Nil	0.08	56.5	59.8	58.2	14.0	19.0	16.5	8.0	2.2	5.1
3989	0.20	0.53		Nil	Nil	0.20	67.0	66.0	66.5	19.5 <sup>a</sup>	45.8 <sup>a</sup>		7.1 <sup>a</sup>	12.5 <sup>a</sup>	
3906	0.24	0.65	0.37	Nil	Nil	0.32	59.2	74.0	66.6	38.0	31.0	34.5	18.2	11.0	14.6
3907	0.20	0.56	0.32	Nil	Nil	0.67	74.0	74.2	74.1	34.0	39.5	36.8	22.8	20.1	21.5
3908	0.23	0.56	0.38	Nil	Nil	0.73	83.5	85.2	84.4	71.5	78.2	74.9	47.5	32.0	39.8

<sup>a</sup> Specimen piped.

Columbium has not been the subject of previous investigation from the standpoint of effect on impact strength. Accordingly, tests were first carried out at room temperature on a series of steels with increasing columbium contents. In order to bring out their notch sensitivity, these

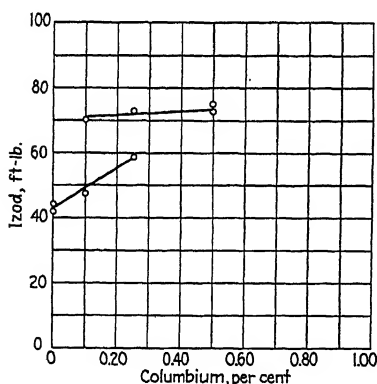


FIG. 4.

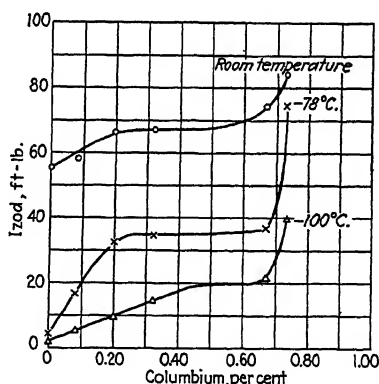


FIG. 5.

FIG. 4.—ROOM-TEMPERATURE IMPACT STRENGTH OF STRAINED AND AGED STEELS WITH VARYING COLUMBIUM CONTENT.

FIG. 5.—AVERAGE LOW-TEMPERATURE IMPACT STRENGTH OF 0.20 PER CENT CARBON-COLUMBIUM STEELS.

steels in the normalized condition were strained 3 per cent and aged 18 hr. at 175° C. Results are shown in Fig. 4 and Table 3. Here again, the energy values fall into two ranges, even though the testing is carried on at room temperature, and the marked progressive effect of increasing colum-

bium content in producing energy values in the upper level is definitely shown. Fig. 5 shows results of a more detailed study of the effect of columbium in plain 0.20 per cent carbon steels normalized as 1-in. dia. bars. The results are noteworthy, in that the impact strength at all temperatures increases with columbium content.

While each of the deoxidizers mentioned above, except titanium, may be used in the proper proportion to obtain the desired low-temperature impact strength of engineering steels, the fact that the aluminum treatment is comparatively inexpensive and is widely used for other purposes makes it particularly interesting from the industrial standpoint. Accordingly, the aluminum-treated steels have been further investigated.

### *Specific Effects of Aluminum Deoxidation*

A variety of aluminum-treated steels was obtained from commercial sources, and a series of impact tests performed at the low temperatures in question. These impact specimens were taken from plates of various sections and various conditions of heat-treatment. While no definite data are available, experience indicates that a lower limit of 10 ft-lb. energy absorption in Izod tests with an implied average of 20 to 40 ft-lb. is sufficient to insure satisfactory performance in pressure vessels and similar structures in services encountered in the petroleum and chemical industries, and the results are judged accordingly. This opinion is also found in the consideration of the Ferrous Materials Committee of the A.S.M.E. Boiler Code Committee in its study of regulations to cover materials for use at low temperatures.

It is appreciated that there is little engineering knowledge with respect to the need for impact strength in any given type of structure. Experience in service is the only criterion of desirable properties. The authors hold no brief for the 10 ft-lb. Izod value chosen as a minimum for purposes of discussion other than to state that it is of the same order of magnitude

TABLE 4.—*Low-temperature Izod Impact Strength of Fifteen Heats of Aluminum-treated S.A.E. 1020-X Steel Heat-treated in 1-inch Diameter Bars<sup>a</sup>*

Temperature of Test	As Forged			Normalized, 900° C.			Normalized, 900° C., Drawn, 650° C.		
	+20° C.	-78° C.	-100° C.	+20° C.	-78° C.	-100° C.	+20° C.	-78° C.	-100° C.
Izod ft-lb.:									
Minimum.....	50.0	23.2	3.5	64.0	40.0	12.2	71.1	9.5	2.6
Maximum.....	80.0	81.8	83.2	81.0	87.0	86.1	83.2	85.0	31.0
Average.....	72.0	54.0	18.8	77.2	70.2	39.6	78.1	36.8	7.9

<sup>a</sup> S.A.E. 1020-X not aluminum-treated gave 40 ft-lb. at room temperature and less than 3 ft-lb. at the low temperatures.

as the minimum set by most experienced engineers and metallurgists in the pressure-vessel field. It is slightly more severe than the 10 ft-lb. Charpy frequently used and incorporated in the A.S.M.E. rules referred to above.

Aluminum-treated S.A.E. 1020-X steel was selected for the first series of tests. The material corresponded to the following chemical analysis:

TABLE 5.—*Low-temperature Izod Impact Strength of Normalized Pipe of Aluminum-treated S.A.E. 1020-X Steel  $\frac{1}{2}$  by 6 Inches Outside Diameter*

Heat-treatment	Number of Tests	Impact Strength, Ft-lb.				
		At +20° C.	At -50° C.	At -78° C.	At -100° C.	At -120° C.
As received....	Average of 2	79.0		80.4	49.5	46.8
Renormalized..	Average of 2	79.4		84.1	85.2	44.1
Stress-relieved..	Average of 8	77.6	71	40.3	21.4	10.4
Stress-relieved..	Minimum	74.2	51	18.2	12.8	6.0

carbon, 0.15 to 0.25; manganese, 0.70 to 1.00; silicon, 0.15 to 0.35 per cent. The tensile strength of the material was approximately 70,000 lb. per sq. in. The McQuaid-Ehn grain size varied in the range of Nos. 5 to 8. One-inch round bars were obtained from 15 different heats. One group was tested as forged, one group as normalized in the 1-in. section, and one group as normalized at 900° C. and drawn at 650° C. in the 1-in.

TABLE 6.—*Low-temperature Izod Impact Strength of Normalized and Stress-relieved  $\frac{11}{16}$ -inch Plate of Aluminum-treated S.A.E. 1020-X Steel*

Direction	Number of Tests	Impact Strength, Ft-lb.				
		At +20° C.	At 0° C.	At -50° C.	At -78° C.	At -120°
Longitudinal..	Average of 10	67.4	68.1	51.5	18.9	4.1
Longitudinal..	Minimum	60.0	60.8	27.5	6.5	2.0
Transverse....	Average of 10	47.4	45.5	24.8	14.3	3.8
Transverse....	Minimum	41.8	42.5	16.2	8.5	1.5

section. Tests were carried out at room temperature, minus 78° and minus 100° C., as shown in Table 4. The as-forged material showed marked reduction of energy absorption at minus 78° C., but the minimum values were still high enough to be considered satisfactory for engineering service. At minus 100° C., however, the values in the as-forged material were so low as to render it unfit for engineering use from this standpoint.



The normalized material showed increased retention of higher values at the lower temperatures, but after normalizing and tempering at 650° C. the values at the low temperatures were seriously reduced. The values were such that the material might be considered just satisfactory at minus 78° C. but definitely unsatisfactory for service at minus 100° C.

TABLE 7.—*Low-temperature Izod Impact Strength of Normalized and Stress-relieved 1½<sup>1</sup>/<sub>16</sub>-inch Plate of Aluminum-treated S.A.E. 1020-X Steel*

Direction	Number of Tests	Impact Strength, Ft.-lb.			
		At +20° C.	At -50° C.	At -78° C.	At -120° C.
Longitudinal.....	Average of 4	65.9	33.4	14.3	3.7
Longitudinal.....	Minimum	60.5	29.5	8.0	2.0
Transverse.....	Average of 4	52.8	26.4	13.8	2.5
Transverse.....	Minimum	48.0	20.0	8.2	2.0

As a further check on the behavior of this material tests were made on specimens taken from ½ by 6-in. O.D. pipe, 1½<sup>1</sup>/<sub>16</sub>-in. plate, 1½<sup>1</sup>/<sub>16</sub>-in. plate and a billet 7-in. square. As welded structures of the type under consideration are usually stress-relieved after welding, most of the tests

TABLE 8.—*Average Low-temperature Izod Impact Strength of 7-inch Square Billet of Aluminum-treated S.A.E. 1020-X Steel<sup>a</sup>*

Heat-treatment	Specimen	Impact Strength, Ft.-lb.					
		At +20° C.	At 0° C.	At -50° C.	At -78° C.	At -100° C.	At -120° C.
As rolled.....	Edge	38.0	27.7	4.7		2.3	1.9
As rolled.....	Center	17.2	7.8	2.5		1.8	1.3
Stress-relieved....	Edge	19.1	9.5	3.6		2.0	1.4
Stress-relieved....	Center	18.7	13.6	3.7		1.6	1.5
Normalized.....	Edge	50.3		17.0	11.5	6.0	3.1
Normalized.....	Center	44.7		15.0	9.8	4.6	3.5

<sup>a</sup> Average of two breaks.

were made after annealing at 650° C. Results of tests on normalized ½ by 6-in. O.D. pipe are shown in Table 5, and indicate that in the as-received and renormalized conditions the pipe is superior to the 1-in. dia. bar described above and satisfies the requirements at minus 120° C. The stress-relieved pipe has adequate impact strength to justify use at temperatures as low as minus 100° C.

Tests on plate in the normalized and stress-relieved condition indicate a definite reduction in the minimum safe temperature as the section increases. The  $1\frac{1}{16}$ -in. plate, as shown in Table 6, is just below the limiting value at minus 78° C. Still further decrease in impact strength is shown by the  $1\frac{9}{16}$ -in. plate, Table 7, as would be expected from the increased mass, and a limiting temperature midway between minus 50° and minus 78° C. is indicated by the criterion herein imposed for suitable engineering performance.

In order to investigate further the effect of mass, specimens were taken from the edge and center of a 7-in. billet. These were tested as received, as stress-relieved, and as normalized. The results of the tests are shown

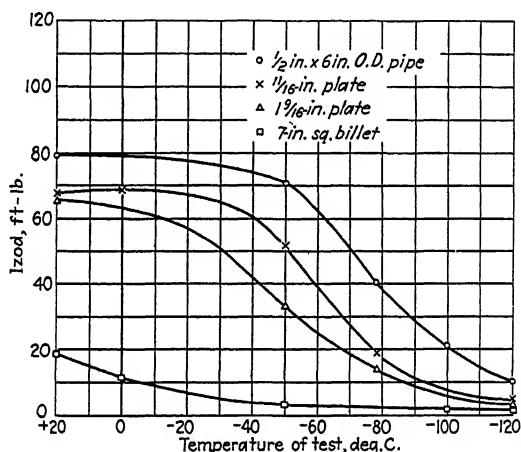


FIG. 6.—EFFECT OF SECTION ON AVERAGE LOW-TEMPERATURE IMPACT STRENGTH OF STRESS-RELIEVED S.A.E. 1020-X STEEL.

in Table 8. The impact strength in the heavier section was substantially lower in all conditions of heat-treatment, both at room temperature and at the low temperatures, and the resulting impact tests indicate that the aluminum-killed S.A.E. 1020-X steel in such heavy sections is generally unsuitable for use at low temperatures.

The effect of mass on the low-temperature impact strength of aluminum-treated S.A.E. 1020-X steel in the stress-relieved condition is summarized in Fig. 6. The longitudinal values of the plate have been used in order to make the plate values consistent with those of the pipe and billet. If a minimum average value of 20 ft.-lb. is taken as the limiting value, the minimum temperatures at which the various sections are safe would be approximately minus 110° C. for the  $\frac{1}{2}$ -in. pipe, minus 80° C. for the  $1\frac{1}{16}$ -in. plate, minus 70° C. for the  $1\frac{9}{16}$ -in. plate and plus 20° C. for the 7-in. square billet. These minimum temperatures may be somewhat optimistic, because of the lower values in the transverse direction.

TABLE 9.—*Effect of Mass on Low-temperature Izod Impact Strength of Aluminum-treated Carbon and Chromium-copper Steels\**

Steel	Section	Heat-treatment	Impact Strength, Ft.-lb.		
			At +20° C.	At -78° C.	At -100° C.
C.....	2 in. sq.	As forged	54.0	10.7	8.3
Cr-Cu.....	2 in. sq.	As forged	68.5	44.4	31.2
C.....	1 in. dia.	Normalized	70.8	51.7	48.5
	2 in. sq.	Normalized	57.9	24.3	18.8
Cr-Cu.....	1 in. dia.	Normalized	77.9	83.6	82.5
	2 in. sq.	Normalized	66.1	54.9	44.6
C.....	2 in. sq.	Normalized and drawn	61.5	22.6	12.3
Cr-Cu.....	2 in. sq.	Normalized and drawn	67.8	59.2	47.9

\* Average of two breaks.

In view of this pronounced effect of mass, an investigation of the effect of alloy additions on mass effect was carried out on plain carbon aluminum-treated steel containing 0.20 per cent carbon, and on aluminum-treated 1 per cent chromium, 0.5 per cent copper, 0.15 per cent carbon steel. These steels were made in the laboratory, and part of each ingot forged to 2 in. square and 1-in. dia. bars. All heat-treatments were

TABLE 10.—*Low-temperature Izod Impact Strength of ½-inch Plate of Aluminum-treated Chromium-copper Steel\**

Heat-treatment	Impact Strength, Ft.-lb.				
	At +20° C.	At -50° C.	At -78° C.	At -100° C.	At -120° C.
As rolled .....	66.3	66.4	64.9	31.5	22.9
Normalized .....	70.5	75.0	61.0	55.8	48.5
Stress-relieved .....	68.3	55.5	30.5	21.5	16.5

\* Average of two values.

carried out in the original forged sections. The results are shown in Table 9. The marked effect of section on reduction of impact strength is clearly evident, as is the effect of the alloy addition in overcoming this mass effect. It is notable that the stress-relieving treatment improved the chromium-copper and harmed the carbon steel. Laboratory heats of 0.75 per cent chromium, 0.50 per cent copper, 0.12 per cent carbon steel were also made and rolled to ½-in. plate. In general, the values, shown in Table 10, even at room temperature are of a lower order than those

found in similar forged heats, and it is probable that the rolling under laboratory conditions was not carried out to the best advantage. However, the impact strength was sufficiently high to meet the limiting value at somewhat less than minus 100° C.

The foregoing experiments show that aluminum treatment substantially increases impact strength of carbon steels at low temperatures, and that it plays the same role in the chromium-copper low-alloy steels. The values obtained indicate that appropriate aluminum-treated carbon steels when used in relatively small sections are suitable for engineering structures operating at temperatures down to approximately minus 100° C. The chromium-copper steel gives impact values indicating that such a steel is suitable for engineering applications involving larger sections at lower temperatures. As the temperatures under investigation in this work include those normally and abnormally encountered in the atmosphere as well as those involved in most of the low-temperature chemical processes now in use, it appears that the fine-grained steels offer a satisfactory solution to the majority of the low-temperature problems now found in industry. However, most of the structures in question involve welded construction, and investigation of the effect of welding on these steels and the impact strength of the weld metal used to join them was considered essential to any broad conclusion.

### PART III. LOW-TEMPERATURE PROPERTIES OF WELDS AND EFFECT OF WELDING ON PLATE

An extensive series of impact tests involving weld metal as well as metal adjacent to the weld was performed, using the aluminum-treated carbon steels as well as the low-alloy chromium-copper steels treated with aluminum. Two well-known commercial electrodes were used. One of these consisted of carbon steel with a mineral coating containing nickel and molybdenum. The other comprised carbon steel with a combustible coating. In addition, tests were performed with a special electrode of the 25-12 chromium-nickel austenitic type of steel with a mineral coating. Depending upon the thickness of the material to be welded, electrodes varied in size from  $\frac{5}{32}$  to  $\frac{1}{4}$  in., and the current density from 100 to 300 amp. Excessive current densities were avoided and after the groove was filled an annealing bead with a small-sized electrode was applied to obtain refinement as near to the surface as possible. Scarfs of the V and U types were prepared for welding the light and heavy material, respectively. Pipe 6 in. in diameter with  $\frac{1}{2}$ -in. wall, and  $1\frac{1}{4}$ -in. and  $1\frac{1}{2}$ -in. plates were selected as representative of the plain carbon, aluminum-treated steels, and were taken from the same lots reported in the previous tests.

One part of each weld in the pipe was tested as welded, part after stress-relieving at 650° C., and part after normalizing at 900° C. Similar

treatments were given to the plate materials as indicated in the tables. One series of standard impact tests was prepared with the notch cut in the weld metal, and another series was prepared with the notch cut at the edge of the weld. In the latter, the base of the notch was at the scarf, the specimen being lightly etched before notching in order to locate

TABLE 11.—*Impact Strength of Welded Pipe of Aluminum-treated S.A.E. 1020-X Steel, ½ by 6 Inches Outside Diameter*  
DIRECTION OF WELD TRANSVERSE TO DIRECTION OF ROLLING

Location	Heat-treatment	Notch	Impact Strength, Ft.-lb.			
			At +20° C.	At -50° C.	At -78° C.	At -120° C.
MINERAL-COATED ROD						
Weld.....	As welded	V	44.5	27.0	15.6	4.4
Weld.....	Normalized	V	56.0	39.5	15.0	6.8
Weld.....	Stress-relieved	V	48.9	35.0	13.8	18.0
Scarf.....	As welded	V	43.1	40.0	60.2	14.5
Scarf.....	Normalized	V	84.0	39.5	19.0	13.8
Scarf.....	Stress-relieved	V	80.2	87.6	88.2	43.5
Weld.....	As welded	Keyhole	25.0	23.8		19.9
Weld.....	Normalized	Keyhole	28.0	17.9		16.0
Weld.....	Stress-relieved	Keyhole	27.0	27.5		20.2
Scarf.....	As welded	Keyhole	24.0	37.0		38.2
Scarf.....	Normalized	Keyhole	23.5	20.8		12.2
Scarf.....	Stress-relieved	Keyhole	34.6	36.0		38.2
COMBUSTIBLE-COATED ROD						
Weld.....	As welded	V	69.0		23.0	31
Weld.....	Normalized	V	72.0	33.2	16.0	4.9
Weld.....	Stress-relieved	V	76.1	48.0	49.0	4.2
Scarf.....	As welded	V	81.6	68.0	84.2	92.8
Scarf.....	Normalized	V	82.0	83.0	83.8	17.8
Scarf.....	Stress-relieved	V	83.4	82.0	63.0	54.9
Weld.....	As welded	Keyhole	27.5	26.4		3.0
Weld.....	Normalized	Keyhole	28.5	24.1		20.0
Weld.....	Stress-relieved	Keyhole	28.0	24.0		20.8
Scarf.....	As welded	Keyhole	36.4	36.0		40.5
Scarf.....	Normalized	Keyhole	32.0	32.0		38.2
Scarf.....	Stress-relieved	Keyhole	37.0	35.5		8.2
MINERAL-COATED "25-12" STEEL ROD						
Weld.....	As welded	V	73.9	80.0	59.1	56.5
Weld.....	Normalized	V	66.2	72.0	55.0	60.0
Weld.....	Stress-relieved	V	81.0	69.2	61.0	60.8
Scarf.....	As welded	V	81.5	82.2	88.8	13.9
Scarf.....	Normalized	V	77.5	82.8	21.0	14.0
Scarf.....	Stress-relieved	V	82.5	48.5	11.0	26.0
Weld.....	As welded	Keyhole	16.8	26.5		25.5
Weld.....	Normalized	Keyhole	30.0	32.0		21.0
Weld.....	Stress-relieved	Keyhole	39.8	36.2		31.9
Scarf.....	As welded	Keyhole	35.0	29.0		37.0
Scarf.....	Normalized	Keyhole	32.5	36.5		39.0
Scarf.....	Stress-relieved	Keyhole	36.0	37.8		35.0

the position. In addition to the standard Izod tests, a series of impact tests using the keyhole notch in the Izod specimen was performed. Tests were carried out at minus 50°, minus 78°, and minus 120° C., and are reported in Table 11. In addition, sections of pipe were flattened at a temperature of 650° C. and other sections were flattened at a temperature of 870° C. These were welded after flattening, the welds running both with and across the direction of the original pipe axis. In this series of experiments, only the mineral-coated steel rods were used, and standard Izod specimens were again prepared with the notch in the weld metal and scarf. The results of these tests are shown in Table 12.

In Table 11, it is shown that both the mineral-coated rod and the combustible-coated rods gave welds with high values at temperatures as low as minus 78° C. Evaluation of the properties at minus 120° C. is

TABLE 12.—*Low-temperature Impact Strength of Flattened Pipe, ½ Inch by 6 Inch Outside Diameter, of Aluminum-treated S.A.E. 1020-X Steel*

Temperature of Flattening, Deg. C.	Direction	Impact Strength, Ft-lb.			
		At +20° C.	At -50° C.	At -78° C.	At -120° C.
Scarf					
650	Longitudinal	48.0	51.8	33.2	17.2
870	Longitudinal	50.5	48.0	44.0	14.8
650	Transverse	92.5	88.2	91.0	52.2
870	Transverse	51.0	72.2	95.6	30.0
Weld					
650	Longitudinal	44.0	30.2	25.5	16.4
870	Longitudinal	39.0	33.8	46.0	16.0
650	Transverse	45.5	27.8	20.8	11.0
870	Transverse	43.0	29.6	33.5	14.2

difficult, as the number of tests was insufficient to establish the proportion of breaks at intermediate and low levels. However, it is apparent that there is little difference and that the best properties were obtained before any heat-treatment. The application of these welds at temperatures lower than minus 100° C. is therefore open to serious question. These results are confirmed by tests on flattened pipe as shown in Table 12, and by tests of welds in  $1\frac{1}{16}$  and  $1\frac{1}{2}$ -in. plate, Tables 13 and 14, respectively. It will be noted that the impact values of the welds themselves are not affected by the section of the base plate. Although the impact strengths were determined at the top and center of the  $1\frac{1}{2}$ -in. welded plate, there was so little consistent difference that the average is considered to be more representative. Taking all of the values into consideration, it would appear that at the lowest temperature, minus 120° C., the mineral-coated rod is slightly superior but the difference is not sufficient to justify

modification of the above mentioned limitation to temperatures above minus 100° C. for welds made with either of these rods. Although the minimum limit of 10 ft.-lb. would permit the application at temperatures as low as minus 100° C., it is doubted whether a general conclusion can be drawn that the material would be safe at minus 100° C. and possibly minus 80° C. might be a more reasonable temperature limit.

It also may be observed that the metal at the scarf is little affected by the welding, and that the change is usually toward higher values, especially in heavier plate. The scarf usually gives a higher value than does either the weld or the base plate and therefore need not be considered

TABLE 13.—Average Impact Strength of Stress-relieved Welded  $1\frac{1}{16}$ -inch Plate of Aluminum-treated S.A.E. 1020-X Steel  
DIRECTION OF WELD LONGITUDINAL TO DIRECTION OF ROLLING

Location	Number of Tests	At Room Temperature	Impact Strength, Ft.-lb.			
			At 0° C.	At -50° C.	At -78° C. <sup>a</sup>	At -120° C.
MINERAL-COATED ROD						
Weld.....	4	50.9	51.2	49.8	36.9	23.4
	Minimum	48.0	48.5	47.8	33.8	19.0
Scarf.....	4	53.1	53.0	45.0	36.3	12.4
	Minimum	50.0	47.8	42.2	25.0	8.8
COMBUSTIBLE-COATED ROD						
Weld.....	4	67.5	64.2	53.3	35.4	11.9
	Minimum	64.0	57.0	37.0	29.0	3.0
Scarf.....	4	58.8	60.8	49.4	30.6	21.2
	Minimum	58.1	59.0	43.2	30.1	12.2

<sup>a</sup> Average of two values.

as a controlling factor. Similarly, hot-forming operations, as illustrated by Table 12, are not critical with respect to temperature and may be performed in the usual manner without harmful effect.

The performance of the austenitic steel rod is of particular interest because the impact strength of the weld is greatly increased and the values in the scarf are either not impaired or are slightly improved. As the plate material under consideration is not superior to the carbon and low-alloy steel welds, the stainless-steel welding rod will not develop its full utility except in conjunction with plate having higher impact strength at temperatures below minus 100° C.

Careful consideration of all of the data presented on welded, plain carbon steel, aluminum-treated, indicates that satisfactory impact

strength may be obtained both on weld metal and scarf at all temperatures down to approximately minus 80° to minus 100° C. At these temperatures and at temperatures still lower, special care is required in the choice of the electrode and welding technique, and special attention must be given to the plate section. Values in the extremely low range

TABLE 14.—Average Izod Impact Strength of Welded 1½-inch Plate of Aluminum-treated S.A.E. 1020-X Steel<sup>a</sup>

DIRECTION OF WELD LONGITUDINAL TO DIRECTION OF ROLLING

Location	Heat-treatment	Impact Strength, Ft.-lb.		
		At +20° C.	At -50° C.	At -120° C.
Weld.....	As welded	37.5	33.9	17.6
Weld.....	Normalized	51.1	33.9	13.1
Weld.....	Stress-relieved	49.0	50.0	32.1
Scarf.....	As welded	27.0	16.1	6.5
Scarf.....	Normalized	29.5	30.4	8.6
Scarf.....	Stress-relieved	31.1	29.1	5.3
COMBUSTIBLE-COATED ROD				
Weld.....	As welded	56.4	41.0	12.5
Weld.....	Normalized	61.5	17.5	3.6
Weld.....	Stress-relieved	61.6	52.5	4.2
Scarf.....	As welded	44.2	19.7	3.1
Scarf.....	Normalized	45.1	15.9	5.3
Scarf.....	Stress-relieved	47.0	31.5	10.1
MINERAL-COATED "25-12" STEEL ROD				
Weld.....	As welded	51.6	43.5	40.8
Weld.....	Normalized	52.3	47.3	41.0
Weld.....	Stress-relieved	52.0	43.4	29.5
Scarf.....	As welded	22.0	8.6	3.3
Scarf.....	Normalized	25.8	8.9	4.8
Scarf.....	Stress-relieved	27.6	11.9	3.0

<sup>a</sup> Average of two tests.

will occur with some frequency at temperatures of minus 100° and minus 120° C. unless all of the factors are carefully studied and appropriate measures taken. The data show that the combustible type of coated rod and the mineral-coated rod are very similar from the standpoint of low-temperature impact properties of weld metal, and that when stress-relieving is involved, as with most structures for engineering application, the type of welding rod giving an austenitic deposit is to be particularly recommended for the lower temperatures.



Earlier work with chromium-copper steel, made without grain-size control, indicated that the impact strength of the scarf was improved rather than harmed by the stress-relieving heat-treatment. Although comparative data to illustrate this point are lacking, in Table 14 are given the scarf properties in the stress-relieved condition of welds in  $\frac{1}{2}$ -in. aluminum-treated steel plate containing 0.75 per cent chromium, 0.5 per cent copper, 0.12 per cent carbon. Even though the plate was of

TABLE 15.—*Low-temperature Izod Impact Strength of Welded and Stress-relieved  $\frac{1}{2}$ -inch Chromium-copper Steel*

DIRECTION OF WELD TRANSVERSE TO DIRECTION OF ROLLING

Location	Type of Rod	Impact Strength, Ft.-lb.				
		At +20° C.	At -50° C.	At -78° C.	At -100° C.	At -120° C.
Scarf.....	Mineral-coated	71.0	71.2	71.5	32.8	15.2
Scarf.....	Combustible-coated	73.0	66.0	79.0	78.0	48.5

doubtful quality, as mentioned above, the impact values of the scarf are of a high order. Although heavier sections of welded chromium-copper steel have not been available for tests, it would appear that the use of the alloy-steel plate will permit utilization of the good properties of the weld metal at temperatures near minus 100° C. in engineering structures requiring sections heavier than  $\frac{1}{2}$ -in. plate.

#### SUMMARY AND CONCLUSION

Notched-bar impact values obtained in steels at low temperatures fall into various energy levels. This phenomenon is a function of the nature of the material and is not due to minor variations in the preparation of the test specimens and test procedure. The nature of the fracture on tensile testing at low temperature shows some correspondence with the discontinuous low-temperature impact values.

Aluminum, vanadium, zirconium and columbium when added to plain carbon or low-alloy steels in sufficient amount to produce grain refinement result in improved retention of impact strength at low temperatures. Aluminum-killed, normalized, plain carbon steels of otherwise appropriate analysis, in small sections are satisfactory for engineering service at temperatures down to approximately minus 80° C. Chromium-copper aluminum-killed low-alloy steels are satisfactory for engineering service at temperatures down to minus 100° C. and may be used in larger sections.

Welds produced with carbon and low-alloy electrodes having a combustible or mineral coating show sufficient energy absorption on low-temperature notched-bar impact testing to indicate their fitness for engineering service at temperatures down to minus 80° C. Material in

the scarf likewise is satisfactory for service down to this temperature. Where lower temperatures or heavy sections are involved, special precaution is necessary in welding, and no general statement is warranted regarding the use of any welding procedure.

This work indicates the broad conclusion that engineering structures such as pressure vessels, pipe etc., can be fabricated with appropriate plain carbon and low-alloy aluminum-killed steels so as to be considered safe for service at the low temperatures commonly encountered in the petroleum and chemical industries.

#### ACKNOWLEDGMENTS

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#### DISCUSSION

(Robert H. Aborn presiding)

MEMBER.—Was there any definite measure of the aluminum content?

W. CRAFTS.—No, on the commercial steels we do not know what the aluminum addition was. The steels had grain sizes of 5 to 6 which would normally be considered as fine-grained steels.

A. V. DEFOREST,\* Cambridge, Mass.—We know, or at least we think we know, that the impact test is sensitive to many factors. One factor is the speed effect of which we do not know a great deal, but which is now becoming much more fashionable. Another is the shape of the notch, the sharpness of the notch, we might say. A third

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factor is the width of the test specimen combined with the sharpness of the notch, which is simply a question of the mechanics by which the material deforms under the notch; and the well-known temperature effect. As we control any of these variables, we change from a brittle fracture to what we call a tough fracture, and to show that any steel is brittle or any other steel is tough is only a matter of choosing a variable which fits the case.

Therefore we must have some idea of the conditions most closely approximating service, what restraint at the notch, what kind of notch, what speed of application of load, and what temperature for the conditions of service which should be simulated in the test from which we are going to choose the steel that is suitable for that service.

I should like to hear more about this 10 ft.-lb. range. Ten foot-pounds under what conditions? It seems to me that we should first discuss what service conditions are, then discuss what variables we are going to put into the test to make it measure the same kinds of conditions that we shall meet in service.

A. B. KINZEL.—We are very much interested in Professor DeForest's discussion and questions. We are still in the same position on the impact testing as we have been with the tensile test for a great many years, that is, that the cart comes before the horse. We have service data. We know that steel which has given service of a definite type does give a certain performance in the test we have chosen to more or less simulate the type of service or to give us some information pertinent to that type of service. There is no absolute connection.

For example, a pressure vessel presumably never actually undergoes shock in the sense of being notched and hit with a hammer with sufficient energy and velocity to simulate an impact test, so we choose a test that we have correlated with service, logically or not, and then tie that test up with further service performance in order to get a limiting value.

As to the various factors involved, we have speed, shape, size and temperature. Mr. Crafts in his presentation did not go into the matter of width of specimen, but a series of tests—a half, three-quarters and full specimens taken singly and jointly—are given in the paper.

As to the shape of the notch, we know that that does determine the susceptibility of the specimen to the test. With change in temperature we get the split in values as a function of this notch sharpness, and the data in the paper on the keyhole notch and the Izod V-notch are pertinent to that. Of course, we choose the temperature which is supposed to be the limiting temperature for the service considered.

As to speed, it seems that within the limits of the usual testing machines there is not a great deal of variation. We know perfectly well that values of the order in use at the Watertown Arsenal cause the picture to change rapidly. But there is no doubt in the minds of many of us that speed and sharpness of notch are combined in one factor which might be called the local rate of loading of the specimen.

As to the 10 ft.-lb., that is selected on the basis of vessels in service, and a few cases of service failures. We know the value of the impact test on the material that failed. We know the value of the impact test for steel in structures which have not failed in service, and then we apply engineering judgment to this service performance and the tests.

We hold no brief for 10-ft.-lb. We prefer 20 ft.-lb. to 10, but service performance leads to the conclusion that 10 ft.-lb. is a safe value.

M. S. NORTHRUP,\* Elizabeth, N. J.—It has been mentioned that there are probably two classes largely interested in impact testing. For the past few years it has appeared

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\* General Engineering Department, Standard Oil Development Co.

that some of us on the consuming end have had to be in both classes. We have had to choose material because of its impact value, and in some cases devise our own methods of test.

The authors are to be commended for the thoroughness with which they have approached their problem. There has been considerable low-temperature work done in the past few years, but it has been of relatively little value to the engineer. Perhaps the most it has accomplished is that it has made many of us conscious of the uncertainty of some of the existing vessels operating at low temperatures, and for that reason the company with which I am associated has, for the last seven or eight years, done considerable low-temperature testing, using the impact value as a measure of the suitability of materials.

While that value, as Dr. Kinzel has said, is of no actual use to the engineer in his design, he can at least select material which at the temperature of service has as high an impact value as he can get.

The 10 ft.-lb. mentioned by Dr. Kinzel and in the paper is based on the Izod test. In our work everything has been done with a Charpy machine, using either the keyhole notch or a milled U notch, with the same base radius as the keyhole notch.

In this work we have made numerous tests on ordinary carbon steels. More recently we have investigated nickel steels, chrome and vanadium and copper-nickel steels, and we have probably arrived at the same conclusions as have most of those doing this type of testing work, that the ordinary carbon steels are of little value to us from the safety standpoint below approximately  $0^{\circ}\text{F.}$ , and the results of tests on both nickel steel and aluminum-treated low-carbon steel indicate that they can perhaps be used down to  $-75^{\circ}$ . The aluminum-treated steels are probably limited to that temperature because of the welding limitations imposed; that is, the welds of that material probably drop very rapidly in impact when you go below  $-75^{\circ}\text{F.}$

In the purchase of pipe and plate, we find a difficulty—that it is impossible to take a standard 10 by 10-mm. specimen. For that reason, we want some kind of specimen for the impact test which is of substandard size.

We have tried various shapes of specimens and have finally come to the conclusion that probably the most useful samples of the substandard size are those in which we cut down the width as mentioned in the paper. But we have also found from our test results, or at least the results have indicated, that the factor to be applied in converting those substandard values to equivalent standard values will vary with the material as well as with what you might call the initial or standard impact values.

In other words, if the material is tested as a standard 10 by 10 specimen and gives a certain value, the factor will be a certain value for a half-width specimen. But if the material is different, the factor will be higher or lower, so that you cannot set up a standard factor for all materials or all the impact values which may arise.

Again I wish to commend the authors on the way they have approached the subject, and the completeness of their data.

A. B. KINZEL.—We appreciate very much the general corroboration given by Mr. Northrup and his work at the Standard Oil Development Co. The matter of the width of specimen is very important, and I hope that we did not give the impression in the paper that this factor should be neglected.

We realize perfectly well, and all those in impact testing have realized it for many years, that the nature of the failure, that is, the amount of it that is shear and the amount that is cleavage or cohesive is determined by the mass factor.

If you have a full cohesive failure, the chances are that the mass factor is 1; that is, a specimen whether it is as wide or half as wide will give the same value as the specimen of standard size. If you have a full shear failure, or something approaching that, the factor probably approaches the geometric ratio.

As to the Charpy and the Izod tests, they are, unfortunately, something that leave us in a quandary, because you cannot establish a Charpy-Izod relationship for steel in general, or for any one steel at any one temperature. As a matter of fact, the relationship changes with the temperature. The steel becomes more sensitive with the Izod notch. Below the initial temperatures the values are lower in the Izod test—whereas above those temperatures the values may be higher.

GUEST.—There has been much criticism of impact tests which is correct, but for the engineer who has to pass on material there is no better test. A forged steel or a rod bar, may give beautiful tensile and elongation test results, and yet may be quite unsatisfactory. But over long experience I have found that the impact test, whether performed in one kind of notch or another, for comparison will eliminate any weak steel. If one takes the tensile test alone, and also in combination with the bend test, it is possible to pass almost any material, bad material as well as good, but with the impact test, the bad material invariably shows up.

In making tests for large engineering firms, I utilized in my own testing division a rapidly manufactured impact test on account of the expense of machining the rectangular impact test. I had all the bars of the machine round, and although my figures were not comparable with outside figures, I could immediately condemn a bad steel which would fail in practice.

The authors are to be congratulated on having made use of this valuable test, and I think that the only disadvantage in its adoption commercially is the cost of machining the rectangular test piece. If we can get a specification for a round impact test piece, we shall have an exceedingly rapid and useful means of sorting out the good and bad material.

A. B. KINZEL.—While we feel that all material to be used at low temperatures should be subjected to the impact test, and are fully cognizant of the usefulness of the test in connection with ordinary boiler plates and such material, many of us do not hold that impact test specifications should be added to ordinary boiler-plate specifications.

The reason is not that we do not feel it would give additional useful information, but that it is an added cost and an added burden, that the information from it will contradict the information in other tests in only a very small percentage of the cases in American practice, and in these few cases the misbehavior of the material will unquestionably show up in the fabrication in the boiler shop. It is for those reasons that many of us have not advocated the incorporation of the impact test into the standard boiler-code specifications.

S. L. HORT,\* Milwaukee, Wis.—The authors bring out considerable new information of a type that is very interesting to manufacturers and users of pressure vessels. I was interested to see that the fracture in the tensile test changes in character at low temperatures, although the authors do not go far in explaining it. I take it they have simply given us the results just as they found them, and with no attempt to explain any discrepancies between what they find and what our conception is of what they should have found. On that account I would like to raise a question—and I do not want to intimate that they are wrong in this, because I do not know—but I notice that while in tests at room temperature, normalizing and stress relieving have about the effect that one would expect, at low temperatures those treatments gave surprisingly low values. It seems to me we ought to have that particular point commented upon considerably more than we have. Both normalizing and stress-relieving are regarded as being beneficial treatments, and here we are confronted with a case in which treatments are definitely bad. That, of course, is assuming that the notch bar test is capable of telling whether the bars are good or bad.

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\* Research Metallurgist, The A. O. Smith Corporation.

The authors have also made a very nice study of notch bar testing, and this paper is of interest in connection with that as well as in connection with the use of these steels.

Some of the steels used are silicon-killed steel, or at any rate they have silicon in them, and presumably are silicon-killed, and subsequently have been treated with the various deoxidizers. Possibly I have missed the point, but it seems to me that the more normal type of plate materials have not been given as complete attention here as have the special steels. If that is so, then I would like to see some work of the same kind done on the more commercial steels, and in that way, compare these results with them.

A. B. KINZEL.—As to a discussion of what you might expect and what we did find, I might say that as far as the split values are concerned, the outcome is pretty much what we anticipated from a number of previous observations that we had made.

The matter of the normalizing and stress relieving after welding is certainly surprising and pertinent. We purposely did not comment on it very much because we need more confirmation and data before we say too much about it. It is significant that the same is not true of the alloy steels. It was true of the aluminum-killed, but not of the alloy steels, which might lead one to the thought that the rapid cooling after welding gives an effective mass effect, which is later destroyed by normalizing and stress relieving. This is not a wholly satisfactory explanation, of course, but it opens up a line of thought at any rate. We hope to have more information on that before too long. It is a very interesting subject.

As to the ordinary rimmed boiler plate, we did not say much about that because we took it for granted that the world at large had accepted the fact that the impact value of such material at approximately zero or slightly below drops to a negligible point. We have a few plain carbon steels in the paper which are silicon-killed, and they, too, drop rapidly.

It is necessary to go to the more complete, shall I say, "deoxidation" of aluminum or columbium, or something of that sort, in order to get the improved characteristics and these occur coincidentally with the appearance of the fine-grained structure.

E. C. WRIGHT,\* Pittsburgh, Pa. (written discussion).—This paper is of considerable interest to us as it correlates work which we have been conducting for the past four years. Our approach to this subject originated along three channels quite independently of each other. Our research laboratory was investigating the characteristics of steels not subject to strain aging at room temperature, and employed low-temperature impact tests as a means of measuring aging characteristics. One of the steel plants was testing a turbidimeter for determining oxygen in open-hearth baths and ladles, and incidentally made low-temperature impact tests on heats produced with varying oxygen contents and different deoxidation treatments. One of our other mills was studying the effect of grain size on low-temperature properties, and made a further series of low-temperature impact tests. Results of these three independent investigations show clearly the influence of deoxidizing treatment and grain size upon the low-temperature impact properties and aging characteristics of the steel. Some of these heats were prepared in laboratory induction furnace melts, but much of the work relates to standard 100-ton open-hearth heats. Up to the present time at least 100 full open-hearth heats have been melted, all of which have shown excellent low-temperature impact properties at temperatures as low as  $-80^{\circ}\text{C}$ . Practically all of this work relates to the SAE 1020-X steel, aluminum-treated.

Results reported on page 563, wherein four specimens of less than standard test-piece width were fractured at a single blow, are interesting, as this type of test verifies results obtained on individual impact test specimens, machined within fractions of

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the standard width. This is an important feature in some industries, especially for pipe and tubing, as in many cases the wall thickness of the pipe is less than the 0.3937-in. width of the standard Izod or Charpy test piece, and it has become customary to cut impact test specimens from tubing which have the full width, three-fourth width, one-half width, or one-fourth width. In all such modified tests the depth of the specimen through the notch is 0.3937 in. Numerous sections broken in these modified widths have shown that the value correlates closely with the value obtained on full-width section impact tests. For example, the impact value obtained on one-half width sections is approximately 50 to 60 per cent of the value obtained on a full-width section. These remarks refer to tests made at subzero temperatures.

Our results on several steels such as SAE 1020-X, SAE 1035, and SAE 1335-X, all aluminum-treated, agree with the authors' finding that the highest Izod values at low temperatures are obtained after simple normalizing of the material. This is prior to machining the test piece. We do find, however, that normalizing the test piece after the preparation of the notch invariably gives higher results than when the samples are normalized prior to machining. This increase in impact value is especially evident in austenitic 18-8 alloys when the specimen is heat-treated after the final machining operation.

Annealing or stress-relieving treatments after normalizing give lower results than the simple normalizing treatment; in some cases very low results are obtained after the specimen is annealed to 650° C. or 700° C. after normalizing. This refers to SAE 1020-X and SAE 1335-X aluminum-treated steels. A reverse condition was found to be true on 2¼ per cent nickel and 3½ per cent nickel steel containing 0.15 per cent carbon. The highest impact values on these steels were obtained with a normalizing treatment of 850° C. followed with 650° C. draw-back temperature.

Investigation of the effect of a series of deoxidizing agents upon a chrome-copper steel is very interesting. Apparently aluminum is the most efficient deoxidizing agent, as indicated by the high impact values obtained on the low-carbon aluminum-treated material. It would have been valuable if this same series of deoxidizing agents had also been applied to plain carbon steels of the SAE 1020-X type. The situation with respect to deoxidizing agents, however, is not entirely clear. We have encountered heats of steel treated with aluminum and containing no silicon, which gave quite erratic impact values. These results occurred on low-carbon steel with approximately 0.12 per cent carbon and 0.50 per cent manganese. The SAE 1020-X steel discussed in the paper contains 0.70 to 1 per cent manganese and 0.15 to 0.30 per cent silicon, in addition to the aluminum treatment. It is believed that the deoxidizing effect of manganese and silicon in some way augments the aluminum treatment. In the case of SAE 1020-X and SAE 1335-X steels, killed with silicon only, very low impact values are obtained at temperatures below -25° C. This agrees with the footnote under Table 4. Since most of our work has been done with standard key-hole Charpy test pieces, we show in Table 16 the maximum, minimum, and average Charpy value of 50 commercial open-hearth heats of SAE 1020-X steel aluminum-treated. This may be useful for comparison with the Izod impact values in Table 4.

The authors' discussion and investigation of the effects of mass on the low-temperature impact properties are quite significant. The data given in Fig. 6 would be of greater interest if the actual grain size of the test specimens cut from the various sizes of the sections had been determined.

The results given indicate clearly that simple low-carbon steels of the SAE 1020-X type properly deoxidized with aluminum should be entirely suitable for temperatures as low as -80° C., even in considerable thickness of section. The striking values exhibited by the chrome-copper type of steel indicate that this analysis can be employed at temperatures as low as -120° C. These temperatures should cover most of the high-pressure work now being conducted at subzero temperatures,

and affords the designing engineer a choice of two well-tested materials of good toughness for such equipment.

TABLE 16.—*Charpy Keyhole Impact Tests on SAE 1020-X Steel Aluminum-treated at Various Temperatures from 1-inch Bars Normalized at 900° C.*

(Values obtained on 50 open-hearth heats.)

Temperature of Test	+24° C. +75° F.	-46° C. -50° F.	-73° C. -100° F.
Minimum.....	35.7	32.3	23.8
Maximum.....	67.3	64.8	55.5
Average.....	51.4	32.3	34.9

W. CRAFTS.—We much appreciate Mr. Wright's generally confirmatory data. His comments on actual grain size are fully justified. We have not investigated it particularly, but will do so. We have found some indication that it is significant in some cases, and in others it is not. We are not sure about the matter of grain size, particularly that fine grain alone does not seem to be the essential for low-temperature impact strength. The amount of residual, metallic deoxidizer present seems to have an effect. We are pleased to learn that Mr. Wright obtained about the same results as far as stress-relieving and annealing are concerned. We wish that he had an explanation, too.

S. J. ROSENBERG,\* Washington, D. C. (written discussion†).—The phenomenon noted by the authors, whereby lowered test temperatures cause apparently erratic results in impact tests of ferrous materials, has also been noted by other investigators of the effect of subzero temperatures upon the impact resistance of steels. In many cases, however, this scatter of test results has been passed over as being the result of experimental error, despite the fact that within certain temperature ranges an error of 100 per cent is not unusual.

As noted by the authors, plausible hypotheses to explain this behavior can be advanced, but they themselves hesitated to do this on the ground that hypotheses not subject to proof would not be particularly constructive. This feeling is to be regretted, since an unproven hypothesis may lead to work which may result in proving that particular hypothesis or developing a newer and truer one.

In the course of a study of the effect of low temperatures upon the mechanical properties of metals, the results of which are as yet unpublished, the writer has observed this scatter of impact-test results at certain temperatures. From a study of the test data it is apparent that this scatter occurs over the so-called "critical temperature range" during which the impact resistance of the particular steel in question decreases more or less markedly as the test temperature is lowered.

It may be noted that this critical temperature range is dependent upon certain variables external to the steel studied as well as the steel itself. Increasing velocities of the hammer, for instance, can move the critical range to higher temperatures. Standardizing upon impact-test conditions, type of notch, etc., leaves the steel itself and the various test temperatures as the only variables.

For the purpose of general discussion, it may be stated that at certain temperatures, usually, but not necessarily, room temperature, the results of impact tests are in sufficiently close agreement to justify the assumption that divergent values are experi-

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† Published with the approval of the Director of the National Bureau of Standards.



mental errors. This same condition also exists at some low temperature, the difference being that at the low temperature the average impact resistance is usually considerably lower than at room temperature. Between these two temperatures, there frequently occurs a marked scattering of impact values from presumably check specimens. The authors have drawn attention to this phenomenon in the first part of their paper and have illustrated it in Fig. 1.

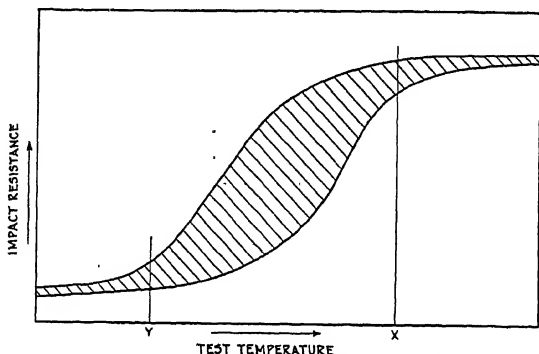


FIG. 7.—EFFECT OF LOW TEMPERATURES ON IMPACT RESISTANCE OF STRUCTURAL STEELS.

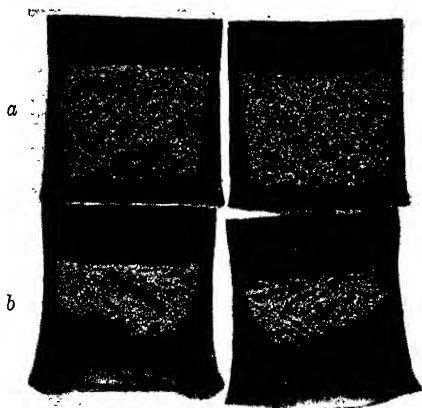


FIG. 8.—FRACTURED ENDS OF DUPLICATE IMPACT SPECIMENS OF NORMALIZED SAE X 4130 STEEL BROKEN AT ROOM TEMPERATURE.  
Original magnification 3; reduced  $\frac{1}{6}$

The general effect of low temperatures upon the impact resistance of structural steels is shown in Fig. 7. The shaded area represents the scatter of test results which may occur. Above temperature  $X$  and below temperature  $Y$  results are usually in fair agreement. Between these two temperatures, however, widely different test results may be secured.

An examination of the fractured surfaces of impact test specimens reveals a certain correlation between their appearances and the shape of the impact-temperature curve. At temperatures above  $X$  the fractures have a dull, fibrous appearance; there is a considerable amount of deformation and the fractures are typical of what is usually referred to as a tough fracture. Below temperature  $Y$  the fractures have a bright, crystalline appearance; there is very little deformation and the fractures are typical

of what is usually referred to as a brittle fracture. Between these two temperatures, fractures having a partly tough and partly brittle appearance are not uncommon.

Fig. 8 shows the fractured ends of duplicate impact specimens of a normalized SAE X4130 steel broken at room temperature. Sample *a* broke with almost an entirely brittle fracture. A small part of the fracture, representing the area occupied by a slight cup and cone at the sides of the fracture and a small area at the bottom, had the characteristics of the tough type of fracture. Thus, about 85 per cent of the area covered by the fracture was of the brittle type and about 15 per cent of the tough type. The impact energy absorbed in breaking was 18.8 ft-lb. (Charpy impact V-notch). Compare this with the check specimen *b*. A thin layer of fibrous appearance exists immediately below the notch. The cup and cone are deeper and there is a considerable amount of deformation at the bottom of the fracture, while in sample *a* there was none. About 60 per cent of the area of the fracture was of the tough type and about 40 per cent was of the brittle type. The impact energy absorbed in breaking was 54.4 foot-pounds.

This same phenomenon was also observed at 0° C. At -20° C., however, and at lower temperatures, only the brittle type of fracture was observed and the impact resistance of all these specimens was relatively low. Four specimens of this steel were also tested at 100° C.; in each specimen the fracture was of the tough type and the impact resistance was high. As a matter of interest, the actual values are given

TABLE 17.—*Charpy Impact, SAE-4130X Normalized*

Test Temperature	-78° C.	-40° C.	-20° C.	0° C.	Room Temperature	100° C.
Foot-pounds.....	4.8	6.6	9.6	45.7	18.8	58.0
	6.8	8.5	12.9	18.8	54.4	58.0
						56.2
						58.0

in Table 17. It is possible that, had tests been made at some temperature between room temperature and 100° C., perfectly good check results would have been secured. Thus it may be concluded that in this particular steel, the so-called "critical range" exists between -20° C. and some temperature higher than room temperature and lower than 100° C. As a matter of safety, it is apparent that only the lower impact values should be used in determining the impact resistance of this steel in the critical range.

Although some writers have advanced very definite ideas as to the cause of low-temperature brittleness, no satisfactory explanation of the cause of both ductile and brittle fractures of check specimens at identical temperatures has been given. The comments of the authors on this subject would be very interesting.

R. K. HOPKINS AND H. S. BLUMBERG,\* Jersey City, N. J. (written discussion).—This paper adds to our knowledge of metals for low-temperature service. The authors are to be commended for the considerable work they have done, and for the detailed analysis of their results.

Nearly all of the low-temperature impact testing which is carried out today is based on the Charpy test. It is well known that the results thus obtained are more consistent than is the case with the Izod test bar, and as a result, practically all specifications which are written require that a certain minimum be obtained upon Charpy bars. However, changes in section which occur in parts for service are neither Izod nor Charpy notches, and it is, therefore, well to have data upon varying kinds of notch.

\* The M. W. Kellogg Company.

It is coincidental that the writers' laboratory has carried out a rather detailed study upon the identical chrome-copper steel used by the authors of the paper in



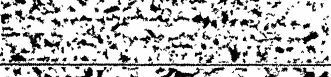






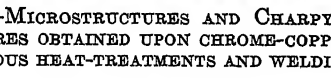
ANALYSIS.			CHARPY IMPACT AVERAGES, FT. LBS.					
C 0.10	Si 0.21	Cu 0.58	TEMPERATURE OF TESTING					
Mn 0.68	Cr 0.77	Ni 0.63						
100X MICROGRAPHS			+70°F		-50°F		-75°F	
ETCHED IN 4% ALCOHOLIC HNO <sub>3</sub>			-112°F		-148°F			
CONDITION			LONG.	TRAN.	LONG.	TRAN.	LONG.	TRAN.
STRESS RELIEVED 1150°F			66.2	57.3	49.6	38.3	44.9	38.2
								31.2
								14.4
								19.3
NORMALIZED 1600°F, STRESS RELIEVED 1150°F			64.3	56.4	60.3	41.4	47.1	43.3
								31.7
								26.5
NORMALIZED 1650°F, STRESS RELIEVED 1150°F			60.6	52.1	54.2	39.4	51.6	38.6
								33.1
								29.9
								24.9
NORMALIZED 1700°F, STRESS RELIEVED 1150°F			61.9	50.5	44.8	33.8	41.9	37.2
								28.8
								33.4
								20.3
NORMALIZED 1750°F, STRESS RELIEVED 1150°F			63.5	52.5	48.2	38.1	42.5	36.7
								28.9
								30.8
								24.8
NORMALIZED 1800°F, STRESS RELIEVED 1150°F			63.4	50.8	47.5	37.1	38.4	37.8
								24.7
								29.4
								3.9
NORMALIZED 1850°F, STRESS RELIEVED 1150°F			60.7	54.4	40.5	33.9	38.9	34.4
								14.0
								4.7
								1.8
NORMALIZED 1900°F, STRESS RELIEVED 1150°F			58.5	47.9	37.7	28.2	33.9	10.3
								28.2
								1.9
								1.7
WELD STRESS RELIEVED 1150°F			23.6		19.4		17.3	16.3
								10.8
ZONE ADJACENT TO WELD STRESS RELIEVED 1150°F			50.7		35.6		48.2	44.4
								37.2

FIG. 9.—MICROSTRUCTURES AND CHARPY IMPACT VALUES AT VARIOUS SUBZERO TEMPERATURES OBTAINED UPON CHROME-COPPER-NICKEL STEEL PLATE  $1\frac{1}{16}$  IN. THICK AFTER VARIOUS HEAT-TREATMENTS AND WELDING, INCLUDING DATA ON WELD AND ADJACENT ZONE.

obtaining the data given in Table 1. Tests were made using the standard Charpy bar, longitudinal and transverse impact bars being prepared from the center of the plate thickness, after which impact tests were made in the temperature range from

plus 70° F. to minus 148° F. The effect of various normalizing heat treatments was also studied, and in addition, the impact properties of weld metal and the heat-affected zone base metal were also obtained. All of these data in which the values given are the average of these tests, together with microscopic structures, are shown in Fig. 9. It will be noted that these data check the report of Dr. Kinzel and his coworkers as to the excellent impact properties which are obtained in metal of this composition down to temperatures as low as -148° F. The interrelation of grain size and good impact properties at the low temperatures is shown in these data by the fact that normalizing temperatures just over the critical range produced small grain size and consequent high impact values. When the normalizing temperatures exceed 1800° F. the grain size increases and the -148° F. impact properties are sharply lowered.

It has been noted also that when many specimens are broken as representative of a given steel in a given condition the results will show differences in "energy level" as pointed out by these investigators. It is to be noted, however, that these differences in Charpy tests are of a lesser degree than in the Izod test.

The company with which the writers are connected has built many large pressure vessels fabricated from chrome-copper-nickel steel, and these vessels are operating satisfactorily at temperatures down to -148° F.

A. B. KINZEL (written discussion).—We appreciate the confirmatory data with attached microstructure and Charpy impact values presented by Messrs. Hopkins and Blumberg. The authors realize full well that the Charpy test gives more consistent results than the Izod under the conditions in question, but believe that the reason for this is that the Izod test is more sensitive and therefore might be considered to be more pertinent to the question at hand. As previously stated in this general discussion, however, the order of magnitude of the values obtained and the general location of the critical temperature are of major interest rather than any of the minor variations in this temperature or the actual values. The impact tests are used to confirm the fact that a given material which we have selected to keep the critical temperature rather low does meet these expectations. Any impact test, Charpy or Izod, which brings out this fact is ample to the purposes in question with low-temperature pressure-vessel service.

We are very much interested in Mr. Rosenberg's discussion and note that the data he gives supplement those given in the paper and lead to the same general conclusions. Mr. Rosenberg wishes us to advance a hypothesis, and an explanation of some of these peculiar phenomena. We agree with him that there might be much value in such a hypothesis. However, in any paper of this type it is necessary to clearly differentiate between fact and hypothesis, and we have preferred to emphasize this differentiation by omitting hypotheses altogether from the paper in question. However, a hypothesis which has been suggested by one of the authors may be found in an article which appeared in the May, 1937 issue of the *Journal of Applied Physics*, presented as a challenge to physicists. We feel sure that the material contained therein is sufficiently speculative and yet sufficiently plausible to satisfy Mr. Rosenberg on this score.



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(NOTE: In this index the names of authors of papers and discussions and of men referred to are printed in SMALL CAPITALS, and the title of papers in *italics*.)

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